70th Anniversary of EPR Discovery

Kazan Federal University
Zavoiskii Physical-Technical Institute
Government of Tatarstan Republic
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MAGNETIC RESONANCE: fundamental research and pioneering applications (MR-70)

Internatonal Conference

MR-70
KAZAN 2014

PROGRAM, ABSTRACTS

Kazan
23-27 June 2014

Kazan Federal University

International Conference “Magnetic Resonance: Fundamental Research and Pioneering Applications”

devoted to the 70-th anniversary of the discovery of Electron Paramagnetic
Resonance by E.K.Zavoiskii

Book of
ABSTRACTS

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The International Conference “Magnetic Resonance: Fundamental Research and Pioneering Applications” is devoted to the 70-th anniversary of the discovery of Electron Paramagnetic Resonance made by E.K. Zavoiskii in Kazan, Russia, on January 25, 1944.

E. K. Zavoiskii

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Conference program

23 June, Monday				
	10.00-10.30	Opening Ceremony	Main Building, Assembly Hall	
	10.30-13.50	***EPR, NMR, AcMR, FMR and AFMR in condensed matter -I***	Institute of Physics, Lecture Hall 110	
Mon 01	10.30-11.00	Scheffler M. (Stuttgart, Germany)		
Mon 02	11.00-11.30	Mukhin A.A. (Moscow, Russia)		
Mon 03	11.30-12.00	Keller H. (Zürich, Switzerland)		
	12.00-12.20	Coffee-break		
	12.20-14.00	***EPR, NMR, AcMR, FMR and AFMR in condensed matter –II*** Institute of Physics, Lecture Hall 110	**Bruker BioSpin Users Meeting** Institute of Physics, Lecture Hall 112	
Mon 04	12.20-12.50	Stern R. (Tallinn, Estonia)	12.20-12.50	U. Eichhoff (Bruker BioSpin GmbH
Mon 05	12.50-13.30	Atsarkin V.A. (Moscow, Russia) Kochelaev B.I. (Kazan, Rusia)	12.50-13.10	D. Moskau (Bruker BioSpin AG)
			13.10-13.30	D. Mathieu (Bruker BioSpin AG)
Mon 06	13.30-14.00	Gippius A.A. (Moscow, Russia)	13.30-13.50	S. Wegner (Bruker BioSpin AG)
	14.00-15.30	Lunch		
	15.30-17.00	***EPR, NMR, AcMR, FMR and AFMR in condensed matter –III*** Institute of Physics, Lecture Hall 110	**Bruker BioSpin Users Meeting** Institute of Physics, Lecture Hall 112	
Mon 07	15.30-16.00	Alloul H. (Paris, France)	15.30-15.50	I. Lubchenko (Bruker Ltd., Moscow)
Mon 08	16.00-16.30	Mikhalev K.N. (Yekaterinburg, Russia)	15.50-16.10	V. Panov (Bruker Ltd., Moscow)
Mon 09	16.30-17.00	Mukhamedshin I.R. (Kazan, Russia)	16.10-16.30	U. Eichhoff (Bruker BioSpin GmbH)
			16.30-16.50	I. Gromov (Bruker BioSpin GmbH)
	17.00-17.20	Coffee-break		
Mon 10	17.20-17.40	Eremin M.V. (Kazan, Russia)	17.20-17.40	M. Kadirov (IOPC KSC RAS)
Mon 11	17.40-18.10	Dzheparov F.S. (Moscow, Russia)	17.40-18.00	S. Orlinskii (Institute of Physics KFU)
Mon 12	18.10-18.30	Dooglav A. (Kazan, Russia)	18.00-18.20	B. Khairutdinov (KIBB KSC RAS)
			18.20-19.20	*Round table*
	19.30-22.00	WELCOME PARTY		

24 June, Tuesday			
09.00-12.50		***Magnetic resonance in medicine*** ***Magnetic resonance imaging***	Institute of Physics, Lecture Hall 110
Tue 01	09.00-09.30	Berliner L. (Denver, USA)	
Tue 02	09.30-10.00	Kaptein R. (Utrecht, Netherlands)	
Tue 03	10.00-10.30	Polshakov V. (Moscow, Russia)	
Tue 04	10.30-11.00	Hennig J. (Freiburg, Germany)	
	11.00-11.20	Coffee-break	
Tue 05	11.20-11.50	Andjus P. (Serbia, Belgrad)	
Tue 06	11.50-12.20	Hirata H. (Japan, Hokkaido)	
Tue 07	12.20-12.50	Mojovic M.D. (Serbia, Belgrad	
13.00-14.30		Lunch	
14.30-16.30		***Magnetic resonance in chemistry and biology***	Institute of Physics, Lecture Hall 112
Tue 08	14.30-15.00	Gescheidt G. (Graz, Austria)	
Tue 09	15.00-15.30	Goldfarb D. (Rehovot, Israel)	
Tue 10	15.30-16.00	Krivdin L.B. (Irkutsk, Russia)	
Tue 11	16.00-16.30	Bowman M. (Tuscaloosa, USA)	
	16.30-16.50	Coffee-break	
16.50-18.10		***Magnetic resonance in medicine, chemistry and biology*** Institute of Physics, Lecture Hall 110	***New technique and methods for magnetic resonance*** Institute of Physics, Lecture Hall 112
Tue 12	16.50-17.10	Usachev K.S. (Kazan, Russia)	Dornich K. (Freiberg, Germany)
Tue 13	17.10-17.30	Il'yasov K. (Kazan, Russia)	Alexandrov A.S. (Kazan, Russia)
Tue 14	17.30-17.50	Kachala V. (Moscow, Russia)	Khasanov R.A. (Kazan, Russia)
Tue 15	17.50-18.10	Izotov V.G. (Kazan, Russia)	Irisova I.A. (Kazan, Russia)
Tue 16	18.10-18.30	Zaripov R.B. (Kazan, Russia)	Nizamutdinov N.M. (Kazan, Russia)
Tue 17	18.30-18.50		Murzakaev V. (Bugulma, Russia)

25 June, Wednesday			
09.00-12.50		***New technique and methods for magnetic resonance*** ***Magnetic resonance at high magnetic fields***	Institute of Physics, Lecture Hall 110
Wed 01	09.00-09.30	Spiess H.W. (Mainz, Germany)	
Wed 02	09.30-10.00	Zvyagin S. (Drezden, Germany)	
Wed 03	10.00-10.30	Ohta H. (Kobe, Japan)	
Wed 04	10.30-11.00	Shengelaya A. (Tbilisi, Georgia)	
	11.00-11.20	Coffee-break	
11.20-12.50		***Magnetic resonance in medicine*** ***Bioinformatics***	Institute of Physics, Lecture Hall 110
Wed 05	11.20-11.50	Lubitz W. (Mülheim, Germany)	
Wed 06	11.50-12.20	Moebius K. (Berlin, Germany)	
Wed 07	12.20-12.50	Sergeev N.M. (Moscow, Russia)	
13.00-14.30		Lunch	
14.30-19.30		EXCURSION TOUR	
19.30-22.00		BANQUET	

26 June, Thursday			
	09.00-11.20	***EPR, NMR, AcMR, FMR and AFMR in condensed matter - IV***	Institute of Physics, Lecture Hall 110
Thu 01	09.00-09.30	Sichelschmidt J. (Dresden, Germany)	
Thu 02	09.30-10.00	Aktaş B. (Gebze. Turkey)	
Thu 03	10.00-10.30	Glazkov V.N. (Moscow, Russia)	
Thu 04	10.30-11.00	Fu M. (Hamilton, Canada)	
	11.10-11.20	Coffee-break	
	11.20-12.50	***Quantum computing and magnetic resonance***	Institute of Physics, Lecture Hall 110
Thu 05	11.20-11.50	Vasiliev S. (Turku, Finland)	
Thu 06	11.50-12.20	Takui T. (Osaka, Japan)	
Thu 07	12.20-12.50	Geru I. (Chisinau, Moldova)	
	13.00-14.30	Lunch	
	14.30-16.10	***Magnetic resonance and nanostructures -I*** Institute of Physics, Lecture Hall 110	***EPR, NMR, AcMR, FMR and AFMR in condensed matter - V*** Institute of Physics, Lecture Hall 112
Thu 08	14.30-15.00	Feldman E.B. (Chernogolovka, Russia)	Sakhratov Yu.A. (Kazan, Russia)
Thu 09	15.00-15.30	Orlinskii S.B. (Kazan, Russia)	Shakurov G.S. (Kazan, Russia)
Thu 10	15.30-15.50	Biktagirov T.B. (Kazan, Russia)	Lisin V.N. (Kazan, Russia)
Thu 11	15.50-16.10	Chernyak A.V. (Chernogolovka, Russia)	Sukhanov A. (Kazan, Russia)
	16.10-16.30	Coffee-break	
	16.30-16.10	***Magnetic resonance and nanostructures -II*** Institute of Physics, Lecture Hall 110	***Magnetic resonance in chemistry and biology*** Institute of Physics, Lecture Hall 112
Thu 12	16.30-16.50	Mashkovtsev R.I. (Novosibirsk, Russia)	Volkov V.I. (Chernogolovka, Russia)
Thu 13	16.50-17.10	Ezhevskii A.A. (Nizhniy Novgorod, Russia)	Safonov A.I. (Moscow, Russia)
Thu 14	17.10-17.30	Yavkin B.V. (Kazan, Russia)	Petr A. (Drezden, Germany)
Thu 15	17.30-17.50	Akdoğan N. (Gebze, Turkey)	Voronkova V.K. (Kazan, Russia)
Thu 16	17.50-18.10	Alakshin E.M. (Kazan, Russia)	Domracheva N.E. (Kazan, Russia)
	18.00-20.00	POSTER SESSION	

27 June, Friday			
	09.00-11.20	***EPR, NMR, AcMR, FMR and AFMR in condensed matter – VI***	Institute of Physics, Lecture Hall 110
Fri 01	09.00-09.30	Bun'kovYu.M. (Grenoble, France)	
Fri 02	09.30-10.00	Khasanov R. (Brugg, Switzerland)	
Fri 03	10.00-10.30	Rameev B.Z. (Gebze, Turkey)	
Fri 04	10.30-11.00	Ivanshin V.A. (Kazan, Russia)	
	11.00-11.20	Coffee-break	
	11.20-12.50	***Magnetic resonance in porous materials and disordered media***	Institute of Physics, Lecture Hall 110
Fri 05	11.20-11.50	Smirnov A.I. (Moscow, Russia)	
Fri 06	11.50-12.20	Klochkov A.V. (Kazan, Russia)	
Fri 07	12.20-12.50	Svistov L.E. (Moscow, Russia)	
Fri 08	12.50-13.20	Dmitriev V.V. (Moscow, Russia)	
	13.30-14.30	Lunch	
	14.30-15.00	Closing	Institute of Physics, Lecture Hall 110
	15.00-19.00	Excursion Tour	

Mon 01 ESR on $YbRh_2Si_2$ at mK temperatures: probing spin dynamics close to a quantum phase transition

M. Scheffler[1], C. Clauss[1], M. Javaheri[1], M. Dressel[1], J. Sichelschmidt[2], C. Krellner[3],
C. Geibel[2], F. Steglich[2]

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The heavy-fermion metal $YbRh_2Si_2$ is a model system for quantum criticality: the very weak antiferromagnetic order below 70 mK can be suppressed e.g. by a small magnetic field of 60 mT. This quantum phase transition results in unusual properties such as pronounced non-Fermi-liquid behavior. Previous ESR studies on $YbRh_2Si_2$ revealed new insights concerning the spin dynamics of this particular material and Kondo lattices in general [1], but were limited to temperatures above 500 mK and could not access the most interesting low-temperature regimes.

We recently developed a new measurement technique [2], based on planar superconducting resonators, which we now use for ESR studies on $YbRh_2Si_2$ single crystals at temperatures down to 40 mK. With a set of ESR frequencies spanning 1.5-13 GHz and ESR fields as low as 30 mT, we address the temperature and field regimes close to the quantum critical point. Our results, with *g* factor and linewidth as the characteristic ESR parameters, cover the three low-temperature, low-field phases of $YbRh_2Si_2$ (antiferromagnet, non-Fermi liquid, field-induced Fermi liquid) and they open new opportunities to gain deeper insight into ESR of heavy-fermion systems and to investigate the quantum critical point.

[1] J. Sichelschmidt *et al.*, Phys. Rev. Lett. **91**, 156401 (2003).
[2] M. Scheffler *et al.*, Phys. Status Solidi B **250**, 439 (2013).

Mon 02 Magnetic resonance in multiferroic rare-earth borates

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Recently rare-earth ferroborates $RFe_3(BO_3)_4$ and alumoborates $RAl_3(BO_3)_4$ have attracted considerable interest due to observation of magnetoelectric effects as well as rich magnetic, optical and other properties which strongly depend on type of the rare-earth (R) ions and their low energy states in the crystal and exchange (R-Fe) fields. Various crystal-field transitions and collective magnetic excitations in antiferromagnetic Fe-subsystem (T_N = 30-40 K) should be responsible for the static magnetic and magnetoelectric properties of the borates. We have investigated these excitations in Tm, Ho… alumoborates and Sm, Nd… ferroborates in the submillimeter (terahertz) frequency range (2-35 cm^{-1}) using quasioptical backward-wave-oscillator spectroscopy.

Low energy crystal-field transitions of Tm^{3+} and Ho^{3+} ions occupying sites of D_3 symmetry in the alumoborates have been observed in the transmittance spectra at low temperatures. According to corresponding selection rules, they have been identified as either magnetic dipolar or electric dipolar transitions. The crystal field states of Tm^{3+} were found to be ground singlet and excited doublet (~28 cm^{-1}) while for Ho^{3+} they represent ground doublet, excited doublet (~12 cm^{-1}) and two excited singlets (~14 and 35 cm^{-1}). Temperature dependencies of the contributions to the permeability and permittivity of these transitions have been obtained and values of the corresponding magnetic and electric dipolar matrix elements have been also extracted. They are in a reasonable agreement with static magnetic and electric susceptibilities. According to the symmetry of the crystal, the field-induced electric polarization in the alumoborates obeys the relations $P_x= \alpha_1 H_y H_z + \alpha_2(H_x^2- H_y^2)+\dots$ and $P_y= -\alpha_1 H_x H_z - 2\alpha_2 H_x H_y+\dots$ for the moderate fields, where $\alpha_1(T)$ and $\alpha_2(T)$ are quadratic magnetoelectric susceptibilities. We have shown that $\alpha_1(T)$ and $\alpha_2(T)$ are also determined by the observed magnetic and electric dipolar transitions and their behavior is in a good agreement with corresponding experimental data. Thus a self-consistent description of the static magnetic, electric and quadratic magnetoelectric susceptibilities based on the spectroscopic data have been carried out for the alumoborates studied.

In the ferroborates the resonance modes originating from excitations in the exchange coupled subsystems of rare earth ions (R = Sm^{3+}, Nd^{3+}…) and Fe^{3+} ions have been detected [1]. The strong interaction between the spin oscillations of the Fe and R subsystems has been revealed, which is determined by the anisotropy of the exchange splitting of the ground doublet of the R ion. It has been shown that the intensities of coupled modes (contributions to the magnetic permeability) depend strongly on the difference between the *g* factors of Fe and R ions that gives a possibility to determine the sign of the latter *g* factor (in particular, we found $g_{\perp,\parallel}^{Nd} < 0$ in $NdFe_3(BO_3)_4$). Among different modes we have found that the lowest in-plane antiferromagnetic resonance mode represents the electromagnon which contributes significantly to the permittivity and determines a giant magnetodielectric effect in $SmFe_3(BO_3)_4$ [2]. Besides this, electromagnon also determines the strong dynamic magnetoelectric effect resulting in the optical activity exceeding 120 degrees of polarization rotation in a millimeter thick sample.

The work is partially supported by RFBR (12-02-01261, 13-02-01093).

[1] A.M. Kuz’menko, A.A. Mukhin, V.Yu. Ivanov, et al., JETP Lett, **94**, 294 (2011).
[2] A.A. Mukhin, G.P. Vorob’ev, V.Yu. Ivanov, et al., JETP Lett, **93**, 275 (2011).

Mon 03

Pressure effects in unconventional superconductors studied by muon spin rotation

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Pressure effect (PE) studies of unconventional superconductors allow one to investigate the role of lattice effects on relevant physical parameters. Muon-spin rotation (μSR) is a powerful and highly sensitive tool for probing static and dynamic magnetic fields in solids on the atomic scale. In type-II superconductors the nanoscale variation of the local magnetic field in the vortex state can be detected by μSR from which the magnetic penetration depth (superfliud density) can be extracted. Furthermore, μSR is a unique microscopic technique to explore magnetic ordering phenomena and various magnetic phases in solids. At the Paul Scherrer Institute (PSI) a high-pressure set-up was realized which allows to perform μSR experiments at hydrostatic pressures up to 25 kbar and low temperatures (~ 0.3 K) [1]. Such experiments open a wide spectrum of new possibilities for investigating the superconducting and magnetic properties of novel materials, such as high-temperature superconductors and related magnetic materials. Here, we present some representative examples of such μSR pressure studies carried out at PSI: Iron-based superconductors turned out to exhibit a rich and complex phase diagram which strongly depends on pressure [2,3]. μSR pressure experiments have significantly contributed to a better understanding of these novel class of superconductors [1,2]. In a further μSR study the PE on the magnetic penetration depth in cuprate superconductors was investigated and found to exhibit an interesting relation to the observed isotope effect [4]. In addition, we performed magnetization and μSR experiments in $La_{2-x}Ba_xCuO_4$ ($x = 1/8$) under hydrostatic pressure, showing that the magnetic volume fraction of the static stripe phase strongly decreases with pressure, while the superconducting volume fraction increases by the same amount [5]. Moreover, we investigated the PE on the magnetic penetration depth in the heavy fermion superconductor $CeCoIn_5$, revealing a strong increase of the superfluid density with pressure [6].

[1] A. Maisuradze *et al.*, Phys. Rev. B **87,** 054401 (2013); M. Bendele *et al.*, Phys. Rev. B **85**, 064517 (2012).
[2] R. Khasanov *et al.*, Phys. Rev. Lett. **104**, 087004 (2010).
[3] M. Bendele *et al.*, Phys. Rev. Lett. **104**, 087003 (2010).
[4] A. Maisuradze *et al.*, Phys. Rev. B **84**, 184523 (2011).
[5] Z. Guguchia *et al.*, New J. of Phys. **15**, 093005 (2013).
[6] L. Howald *et al.*, Phys. Rev. Lett. **110**, 017005 (2013).

Mon 04 Magnetic frustration in $BaCuSi_2O_6$ released

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Han Purple ($BaCuSi_2O_6$) is not only a remarkable ancient pigment, but has also served physicists as a valuable model material for studying Bose-Einstein condensation (BEC) of magnons in high magnetic fields. We have characterized the BEC phase by copper and silicon NMR at 50 mK and around 23-27 T [1]. In parallel, we have succeeded to establish low-T structural model of $BaCuSi_2O_6$ via scattering techniques at PSI. Using these precise low-temperature structural data and extensive density-functional calculations, we elucidate magnetic couplings in this compound. The resulting magnetic model comprises two types of nonequivalent spin dimers, in excellent agreement with the $^{63,65}Cu$ nuclear magnetic resonance data. We further argue that leading interdimer couplings connect the upper site of one dimer to the bottom site of the contiguous dimer, and not the upper-to-upper and bottom-to-bottom sites, as assumed previously. This finding is verified by inelastic neutron scattering data and implies the lack of magnetic frustration in $BaCuSi_2O_6$, thus challenging existing theories of the magnon BEC in this compound.

[1] V.V. Mazurenko, M.V. Valentyuk, R. Stern , and A.A. Tsirlin. Nonfrustrated Interlayer Order and its Relevance to the Bose-Einstein Condensation of Magnons in $BaCuSi_2O_6$. Phys. Rev. Lett. **112**, 107202 (2014).

Mon 05 Low-frequency and dc phenomena in magnetic resonance

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A review is given of some low-frequency and dc magnetic-resonance phenomena studied by the authors and their co-workers since 1970's up today. The content includes: the enhanced longitudinal susceptibility effect (ELSE) based on the concept of the dipole-dipole reservoir in EPR; direct registration of NMR in rotating frames; modulation method of measuring extremely fast electron-spin longitudinal relaxation; resonance spin rectification ("spin dynamo"), resonance magnetoresistance, and magnetic pseudoresonance (a giant peak of r.f. absorption) in conducting ferromagnetic films. Physical mechanism of these effects, as well as applications in studying spin dynamics and relaxation in solids, including high-temperature superconductors, rare-earth manganites, etc., are considered.

Mon 05 Magnetic properties and spin dynamics of superconducting cuprates near the phase transition

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Distortion of the long-range antiferromagnetic order in the underdoped cuprates$YBa_2Cu_3O_{6+y}$ was investigated by the EPR measurements for $y = 0.1 - 0.4$ using Yb^{3+} ions as the EPR probe. An effectiveness of this method was demonstrated previously [1]. In weekly doped samples with $y = 0.1$ a strong anisotropy of the EPR linewidth is revealed for the parallel and perpendicular orientations of the external magnetic field relative to the tetragonal symmetry axis. It was proposed that this anisotropy is related to the indirect spin-spin interaction between the ytterbium ions via antiferromagnetic spin-waves. The explicit expressions for the coupling of ytterbium ions with the spin waves and the corresponding indirect spin-spin interactions were derived. An estimate of the exchange coupling between the ytterbium and copper ions was found from the comparison of the theory with the experiment. In the case of the doping level $y = 0.2, 0.3$ the EPR signal consists of narrow and broad lines, which we relate to formation of the charged domain walls. Our theoretical analysis of the inhomogeneous EPR broadening due to the local AF order distortion in domain walls is well consistent with experimental results for the case of coplanar elliptical domain walls. We discuss also a possible origin of the strong isotope effect of the phase transition temperature in the case of underdoped cuprates.

[1] A. Maisuradze, A. Shengelaya, B.I. Kochelaev, E. Pomjakushina, K. Conder, H. Keller, K.A. Müller. Probing the Yb^{3+} spin relaxation in $Y_{0.98}Yb_{0.02}Ba_2Cu_3O_x$ by electron paramagnetic resonance. Phys. Rev. B **79**, 054519 (8pp) (2009)

Mon 06 Nuclear resonance spectroscopy of strongly correlated Fe-based intermetallic compounds

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The small gap Fe-based semiconductors FeSi, $FeSb_2$ and $FeGa_3$ attracted much interest because of their prospective thermoelectric applications and intriguing low-temperature properties. They represent a rare class of non-magnetic and semiconducting Fe-based intermetallic compounds characterized by a small hybridization gap of about 0.5 eV at the Fermi level [1,2]. The formation of the energy gap in these 3*d*-materials is reminiscent of that in strongly correlated 4*f* Kondo-insulators. Because of the small value of the energy gap and narrow energy bands, these compounds are considered as potential thermoelectric materials demonstrating extremely high Seebeck coefficient values of $|S| \approx 500$ µV/K at 50 K and $|S| \approx 45$ mV/K at 10 K for FeSi [3] and $FeSb_2$ [4], respectively.

Here we present an overview of application of NMR, NQR and spin-lattice relaxation measurement technique in study of electronic and magnetic properties of strongly correlated Fe-based intermetallic compounds $FeSb_2$ and $Fe_{1-x}Co_xGa_3$. Special attention is focused on NMR evidence of the in-gap states formation in $FeSb_2$ and $FeGa_3$. Also nuclear resonance spectroscopy enables to track an evolution of crystal structure, electronic and magnetic properties with Co substitution for Fe in $Fe_{1-x}Co_xGa_3$ solid solution [5,6]. In particular, in the parent compound $FeGa_3$ the ^{69,71}Ga spin-lattice relaxation rate $1/T_1(T)$ reveals an unexpected huge maximum at low T with an essentially magnetic relaxation mechanism indicating the existence of the in-gap states. The other end binary compound, $CoGa_3$, is a band metal. It demonstrates the metallic Korringa behavior of the spin-lattice relaxation with $1/T_1 \sim T$. Surprisingly, in the intermediate $Fe_{0.5}Co_{0.5}Ga_3$ compound $1/T_1(T)$ is strongly (by ~ 2 orders) enhanced due to antiferromagnetic (AF) spin fluctuations with $1/T_1 \sim T^{1/2}$ in perfect agreement with Moriya's spin-fluctuation theory [7] for itinerant magnetic systems. Such a $1/T_1(T)$ behavior is a unique feature of weakly and nearly AF metals.

This work was partially supported by the RFBR Grant №14-03-31181 mol_a; joint Russian-Taiwan Grant RFBR-NSC № 12-03-92002-NSC_a (101-2923-M-006-001-MY2) and Deutsche Forschungsgemeinschaft (DFG) via TRR 80 (Augsburg-Munich).

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Mon 07

NMR study of the superconducting gap variation near the Mott transition in Cs_3C_{60}

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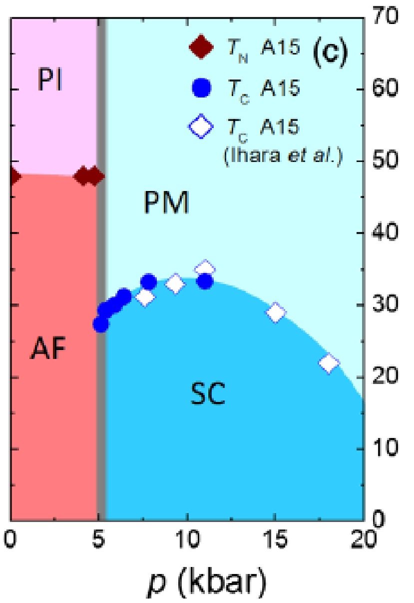
Former extensive studies of superconductivity in the A_3C_{60} compounds, where A is an alkali metal, have led one to consider that Bardeen-Cooper-Schrieffer electron-phonon pairing prevails in those compounds [1]. Among various evidences many came from NMR studies [2].

While this has led to consider that electronic correlations were not important, further detailed studies of A_nC_{60} compounds with n =1, 2, 4 [3,4] gave evidences that their electronic properties cannot be explained by a simple progressive band filling of the C_{60} six-fold degenerate t_{1u} molecular level. This could only be ascribed to the influence of electron correlations and of Jahn-Teller Distortions of the C_{60} ball, which energetically favour evenly charged C_{60} molecules [3].

The discovery of two isomeric fulleride compounds Cs_3C_{60} which exhibit a transition with pressure from a Mott insulator (MI) to a superconducting (SC) state clearly reopened that question [5,6]. Using pressure (p) as a single control parameter of the C_{60} balls lattice spacing, one can now study the progressive evolution of the SC properties when the electronic correlations are increased towards the critical pressure p_c of the Mott transition.

We have used ^{13}C and ^{133}Cs NMR data taken on the A15-Cs_3C_{60} cubic phase, just above p_c = 5.0(3) kbar, where the SC transition temperature T_c displays a dome shape with decreasing cell volume [7]. From the T dependence below T_c of the nuclear spin lattice relaxation rate $(T_1)^{-1}$ we determine the electronic excitations in the SC state, that is 2Δ, the gap value. The latter is found to be largely enhanced with respect to the Bardeen-Cooper-Schrieffer value established in the case of dense A_3C_{60} compounds. It even increases slightly with decreasing p towards p_c, where T_c decreases on the SC dome, so that $2\Delta/k_BT_c$ increases regularly upon approaching the Mott transition. These results bring clear evidence that the increasing correlations near the Mott transition are not significantly detrimental to superconductivity. They rather suggest that repulsive electron interactions might even reinforce electron-phonon superconductivity, being then partly responsible for the large T_c values, as proposed by theoretical models taking the electronic correlations as a key ingredient [8].



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Mon 08 NMR study of the orbital order in $LaMnO_3$

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The oxide $LaMnO_3$ is the parent compound of the colossal magnetoresistance manganites [1] and it is considered a textbook example of a cooperative Jahn-Teller (JT) orbitally ordered material [2].

The Mn spin correlations and the charge distribution were studied near the *O' - O* phase transition at T_{JT} = 750 K up to 950 K with ^{17}O and ^{139}La NMR in a stoichiometric $LaMnO_3$ crystalline sample. The measured local hyperfine fields originate from the electron density transferred from the e_g and t_{2g} orbitals to the 2*s*(O) and 6*s*(La) orbits, respectively. By probing the oxygen nuclei, we show that the correlations of the Mn spins are ferromagnetic in the *ab* plane and robust up to T_{JT}, whereas along the *c* axis they are antiferromagnetic and start to melt below T_{JT}, at about 550 K. Above T_{JT}, the ferromagnetic Mn-Mn exchange interaction is found isotropic. The room-temperature orbital mixing angle, $\varphi_{NMR} = 109^o$, of the e_g ground state is close to the reported value which was deduced from structural data on Jahn-Teller distorted MnO_6 octahedra [3]. For $T > T_{JT}$, $LaMnO_3$ can be described in terms of nonpolarized e_g orbitals since both e_g orbitals are equally occupied.

The ^{17}O spin-spin relaxation time, $^{17}T_2$, which shed light on the low-frequency dynamics of the Mn spins, shows different behavior at the nonequivalent oxygen sites: O2 (in the *ab* plane) and O1 (along the *c* axis). Indeed, at the O2 site, $^{17}T_2$(O2) is constant up to T_{JT}, while at the O1 sites, $^{17}T_2$(O1) data evidence that above 550 K, slow fluctuations of the Mn spins along *c* are thermally activated. Collective modes of adjacent octahedra along the *c* axis should be considered for this slow mechanism which yields changes of the spin correlations between adjacent Mn along *c*, a spin marker of the orbital ordering.

This work is supported by the RFBR Grant No 12-02-00358 and the UB RAS Research project No 12-Y-2-1025.

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Mon 09 Na order and cobalt charge disproportionation in sodium cobaltates Na_xCoO_2

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The influence of the dopant atoms on the electronic properties of conducting layers in complex layered oxides of transition elements is one of the most intriguing questions in strongly correlated electrons physics. This influence is under strong debates now in HTSC cuprates, while there are many experimental evidences in the sodium cobaltates Na_xCoO_2 for a large interplay between the Na atomic ordering and the electronic density on the Co sites. NMR experiments and structural investigations in the cobaltates have given evidence that for $x>0.5$ a large interplay occurs between atomic arrangements and electronic properties, as the Na atoms are found to be ordered [1].

The rich phase diagram of sodium cobaltates include ordered magnetic states, high Curie-Weiss magnetism and metal insulator transition, superconductivity *etc*. The Na_1CoO_2 compound is a band insulator in which the Co sites are in filled-shell nonmagnetic Co^{3+} states. At $x<1$ the system becomes metallic, but only specific Na compositions can be obtained, which correspond to some Na orderings as observed by diffraction techniques. For $x=0.5$ the Na atoms are ordered in an orthorhombic superstructure commensurate with the Co lattice. As a consequence small charge disproportionation into $Co^{3.5\pm\varepsilon}$ with $\varepsilon<0.2$ occurs. In another peculiar phase with $x=2/3$ the ordering of the Na atoms on the hexagonal substructure is rather simple and results in a differentiation of the Co sites into non-magnetic Co^{3+} sites and a metallic Kagome network of Co sites on which the doped holes are delocalized [2].

Among the phases which exhibit a low T magnetic order, a prevalent attention has been paid to the phase with a well defined Néel temperature of $T_N=22$ K. This phase appears to be one of the most stable magnetic phases of sodium cobaltates, which has been found by many researchers. Our recent ^{23}Na NMR study of this sodium cobaltate phase allowed us to demonstrate that the two-dimensional structure of the Na order corresponds to 10 Na sites on top of 13 Co sites unit cell, that is with $x=10/13\approx0.77$ [3]. At the same time we have demonstrated the difficulties in producing homogeneous uniform samples of this cobaltate phase. To perform ^{59}Co NMR study of this phase single crystals of sodium cobaltates Na_xCoO_2 with $x\approx0.8$ were grown by the floating zone technique. Using electrochemical Na de-intercalation method we reduced the sodium content in the as-grown crystals down to pure phase with 22 K Néel temperature. The ^{59}Co NMR study in the paramagnetic state of the phase permitted us to evidence that at least 6 Co sites are differentiated. They could be separated by their magnetic behaviour into three types: a single site with cobalt close to non-magnetic Co^{3+}, two sites with the most magnetic cobalts in the system, and the remaining three sites displaying an intermediate behaviour. This unusual magnetic differentiation calls for more detailed NMR experiments on our well characterized samples.

This work was partially supported by the RFBR under project 14-02-01213a. I.F.G. thanks for support the Ministry of Education and Science of the Russian Federation.

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Mon 10

Magnetic properties of rare-earth ions with orbital degenerate states

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Our study is motivated by recent experimental data about unusual properties of new compounds such as $PrTr_2Al_{20}$, where Tr = Ti,V [1]. Pr^{3+} has cubic site symmetry and a nonmagnetic ground doublet ${}^3H_4(\Gamma_3)$. The interaction of Γ_3 state with magnetic field arises via excited Γ_4 state and can be described by the effective operator:

$$H_{eff} = -7\frac{(\mu_B g_J)^2}{3\Delta_{\Gamma_4}}\left[2\left(H_x^2 + H_y^2 + H_z^2\right)U_A - \left(2H_z^2 - H_x^2 - H_y^2\right)U_\theta - \sqrt{3}\left(H_x^2 - H_y^2\right)U_\varepsilon\right].$$

Here g_J is Lande factor, U_A, U_θ and U_ε are Pauli–like operators acting within orbital degenerate states $|\theta\rangle = \frac{1}{\sqrt{24}}\left[\sqrt{7}\left(|4\rangle + |-4\rangle\right) - \sqrt{10}\,|0\rangle\right]$ and $|\varepsilon\rangle = \frac{1}{\sqrt{2}}\left[|2\rangle + |-2\rangle\right]$:

$$U_A = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix},\ U_\theta = \begin{vmatrix} -1 & 0 \\ 0 & 1 \end{vmatrix},\ U_\varepsilon = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}.$$

We focus here on interesting peculiarity on such compounds. The magnetic dipole–dipole interaction vanishes. However, it can be induced by the external magnetic field. Indeed, combining operator of magnetic dipole–dipole interaction and Zeeman energy operator one gets:

$$H_{eff}^Z = -32\frac{(\mu_B g_J)^4}{\Delta_{\Gamma_5}^2 R_{il}^3} H_Z^2 (U_A^i + U_\theta^i)(U_A^l + U_\theta^l)$$

For the case, when magnetic field is directed along the x axis we have:

$$H_{eff}^Z = 4\frac{(\mu_B g_J)^4}{\Delta_{\Gamma_5}^2 R_{il}^3} H_x^2 [3U_\varepsilon^i U_\varepsilon^l + (2U_A^i - U_\theta^i)(2U_A^l - U_\theta^l) + \sqrt{3}U_\varepsilon^i(2U_A^l - U_\theta^l) + \sqrt{3}U_\varepsilon^l(2U_A^i - U_\theta^i)].$$

As one can see, it can be interpreted as an operator of quadrupolar–guadrupolar interaction induced by external magnetic field. It is clear that this interaction will shift the critical temperature of guadrupolar order, and the shift is proportional to the square of the applied field. I shall argue that this effect can be observable. I shall also discuss peculiarities of Kondo–like and M.M. Zaripov–like interactions in such compounds, which are also quite unusual.

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Mon 11 Magnetic resonance and relaxation of polarized beta-active nuclei. Modern state and visible trends

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A review of experimental and theoretical studies in magnetic resonance and relaxation of polarized beta-active nuclei (beta-NMR) is presented since invention of the method just after discovery of parity nonconservation. Main attention will be devoted to studies of ITEP group and following topics will be discussed:

1. Basics of the method and layouts of reactor- and accelerator-based installations.
2. Applications for nuclear physics studies.
3. Main differences and advantages of beta-NMR relative to conventional NMR in studies of condensed media.
4. Studies of radiation damages, accompanying creation of polarized beta-active nuclei in solids. Quadrupole interactions in crystals.
5. Precision measurements of NMR form-function.
6. Multi-spin and multi-quantum resonances.
7. Resonance at double Larmor frequency in studies of dislocations and spin dynamics in disordered spin system.
8. Delocalization of nuclear polarization in a model disordered spin system ^{8}Li-^{6}Li (spin version of Forster resonance energy transfer) and random walks in disordered media.
9. Accelerator-based beta-NMR investigations of surfaces and interfaces – modern works from TRIUMF (Canada).
10. Expected studies in nearest future on reactor- and accelerator-based installations.

Mon 12

Zavoiskii and NMR: The analysis of the logbooks and rerunning of the experiments

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The laboratory logbooks of E.K. Zavoiskii, the discoverer of Electron Paramagnetic Resonance, to the 70-th anniversary of which this Conference is devoted, evidence that a lot of attempts to observe NMR in condensed matter were done by him. The time from the beginning of 1941 and up to the beginning of the war in June 1941, was devoted completely to the search of NMR in different samples and of different nuclei. Later, studying the relaxation absorption in paramagnetic salts and their solutions, Zavoiskii regularly returned back to NMR.

This report is devoted to the analysis of Zavoiskii's chances to discover continuous wave NMR at least a year earlier than it has been done by Robert V. Pound, Edvard M. Purcell and Henry C. Torrey on Saturday, December 15, 1945. The results of the analysis are confirmed by the rerunning of Zavoiskii's NMR experiments in different conditions.

Tue 01 Early history, developments and the future in magnetic resonance applications to biology and medicine

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This lecture is a personal account of the early history and developments of spin labeling and in-vivo EPR and their applications to biology and medicine. It begins with the move of Professor Harden McConnell from the California Institute of Technology to Stanford University and the earlier work and interactions that triggered the start of the application of aminoxyl radicals (nitroxide) to applications to biology and medicine. Some of the reminiscences reflect a graduate student starting his research as this area evolved. While applications of magnetic resonance (NMR and EPR) had been attempted earlier by some real pioneers in our field, it was probably the spin labels that gave the EPR applications more versatility and sensitivity than had been possible in the past. The general area of magnetic resonance applications to biology and medicine certainly expanded in the 1980s onward and has exploded ever since.

The promises for the future are, as always, technology/instrument dependent but also critically dependent on synthetic organic chemistry to develop the versatile, specific labels and probes for the biological or medical problem at hand. While MRI/NMR have the advantage of naturally occurring isotopes of suitable abundance, EPR cannot enjoy that benefit. In addition, the application of microwave energy to living, lossy samples presents some major safety and sensitivity problems. Of course, the ‘marriage’ between the two techniques is one of the answers.

In conclusion, the talk presents some of the author’s ideas, predictions and wishes for methodologies to develop that would be even more powerful than what we have today.

Tue 02 Protein-DNA recognition: how does the protein finds its target?

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The *E.coli* lac repressor is a text-book example of a bacterial gene regulatory protein. Our NMR studies of the structure and dynamics of complexes of a dimeric lac headpiece with lac operator DNA have provided a detailed picture of how the various lac operator sequences are recognized [1]. Furthermore, interactions with anon-operator DNA have also been elucidated [2]. Generally, these non-specific interactions are assumed to be crucial for rapid target-site location by DNA-binding proteins. The NMR structure of the non-specific lac headpiece-DNA complex clarified how the repressor searches for its target site by sliding along random DNA and binds to the operator through a folding-coupled-to-binding transition [2]. However, surprisingly the 1D diffusion rates for sliding on DNA obtained from NMR are much slower than those determined by single molecule fluorescence methods and cannot account for an enhanced target location by lac repressor [3].In the lecture I will discuss possible reasons for this discrepancy.

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Tue 03 NMR studies of protein-ligand interactions

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Studies of the molecular recognition processes are essential for understanding the mechanism of numerous biochemical processes in a live organism, as well as for developing new rational approaches to the design of new biologically active compounds. Developments of new hardware and techniques in the last decades have strengthened position of NMR spectroscopy as one of the most powerful and informative biophysical methods of biological macromolecule structure determination and elucidation of protein-ligand interactions. NMR spectroscopy gives ample opportunities for studying protein-ligand interactions. Some of such opportunities will be illustrated in the present report with the results of our ongoing studies. The report will briefly describe some of the basic principles involved in studies of protein–ligand interactions and identify the range of possible applications.

One concept assumes structure determination of a protein-ligand complex in solution using the methods of NMR spectroscopy. Moreover NMR techniques allow also to identify specific protein-ligand interactions and to study dynamic properties of a complex in broad timescale of internal motions. This approach will be illustrated by the results of studies of highly specific interaction of bacterial dihydrofolate reductase with its inhibitor - an antibacterial drug trimethoprim, and also by the results of our ongoing studies of zinc ion interaction with the metal binding domain of β-amyloid peptide, involved in the development of the Alzheimer’s disease.

Another “chemical shift mapping” approach is based on the analysis of protein chemical shift changes caused by interaction with ligands. Interacting protein residues can be identified and mapped on the surface of a known protein structure. This will be illustrated by the studies of mRNA stop codon recognition by the human translation termination factor eRF1. Approach similar by the concept was also used for the determination of the interaction interface of the middle domain of human eRF1 with the large subunit of eukaryotic ribosome.

Third approach assumes use of NMR spectroscopy as a tool of qualitative screening of pharmaceutical libraries to assess specific binding of the ligands to target protein. In contrast to the approaches mentioned above, NMR screening techniques are based on the detection of spectral parameters of ligands instead of protein. Therefore it increases sensitivity of such NMR techniques, allows reducing concentration of studied protein and removes need of its highly expensive isotope labeling. Opportunities of modern NMR screening techniques will be illustrated with the results of our ongoing studies aimed at the design of the inhibitors of methionine γ-lyase – an important potential antibacterial drug target.

This work was partly supported by the Russian Foundation for Basic Research (grants 14-04-00477-a and 13-04-40108-H).

Tue 04 New horizons in spatial encoding in MRI

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Tue 05 MRI studies on ALS animal models

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Amyotrophic lateral sclerosis (ALS) is a devastating neurological disorder affecting upper and lower motoneurons. Magnetic resonance imaging (MRI) is the only non-invasive technique that provides structural information on cell loss, metabolic changes and state of the blood brain barrier (BBB) altogether. Reliable biomarkers in ALS are still lacking. For further research progress reliable animal models are needed. To this aim we have used the clinical MRI to assess neurodegenerative processes in the hSOD-1^{G93A} ALS rat model. T2- or T1-weighted MRI protocols were used with a mini surface coil placed over the skull of the anesthetized animal in a 1.5 or 3.0 T wide bore magnet. Since immune misbalance is known to be an important manifestation of the disease we were particularly interested in following the immune cells labelled by paramagnetic nanoparticles (USPIO) in the familial ALS rat model, hSOD-1^{G93A}. Foci of neuroinflammation were also checked by immunofluorescence of microglia (ED1 and OX42) and astrocytes (GFAP) and confocal laser scanning. It was confirmed with Gd-DTPA contrast that the BBB is compromised at the interbrain level. This justified the study of immune cell infiltration by i.v. injecting the rats with magnetically labelled antibodies (MACS® technology) against helper CD4+ or cytolytic CD8+ killer T cells. By combined T1, T2 and T2* weighted imaging of ALS rat brains CD4+ lymphocyte infiltration was observed in the brainstem-midbrain region (Fig. 1) while the CD8+ cells were more confined to the brainstem region.

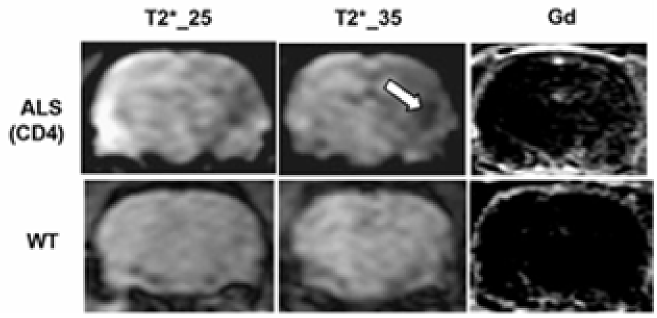

Figure 1. Example of MRI scans of the ALS rat brain with anti-CD4 (interbrain) USPIO antibodies as compared to control WT scans. Note hypointense signal void in ALS that is more intense with Time to Echo 35 ms (arrow). "Gd" – difference of images with and without Gd-DTPA contrast – hyperintensities indicate BBB leakage.

Immunocytochemistry revealed reactive astrocytes (GFAP staining) in the vicinity of dilated lateral ventricles, and microglial activation (OX42 staining) in the ALS rat hippocampus and brainstem. In the latter structures it was also noted that OX42-positive granules appear or a homogeneous cytoplasmic stain occurs in neurons labelled by NeuroTrace. Moreover, macrophage antigen ED1 showed a colocalization with SOD1 overexpressing cells in the ALS brainstem.

These studies reveal complex inflammatory processes in diverse regions of the ALS brain not only residing in motoneuronal nuclei. The use of Gd-based contrast agents for the BBB with paramagnetic antibodies for immune cells offers translational value for diagnostic nanotechnology.

Tue 06 In vivo tumor extracellular pH monitoring using EPR spectroscopy

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In this study, we assess the viability of CW-EPR spectroscopy with a pH sensitive nitroxide to measure extracellular tumor pH (pH_e) in the mouse model. 750-MHz CW-EPR spectroscopy of C3H HeJ mice hind leg squamous cell tumor was performed after intra-venous tailvein injection of pH sensitive nitroxide (R-SG, Fig. 1) during stages of normal tumor growth, and in response to a single 10Gray (Gy) dose of X-ray irradiation. An inverse relationship was observed between tumor volume and pH_e whereby during normal tumor growth a constant reduction in pH_e was observed (Fig. 2). This relationship was disrupted by X-ray irradiation, and from 2-3 days post exposure, a transitory increase in pH_e was observed. In this study, we demonstrated the viability of CW-EPR spectroscopy using R-SG nitroxide to obtain high sensitivity pH measurements in mouse model tumor with an accuracy < 0.1 pH units [1].

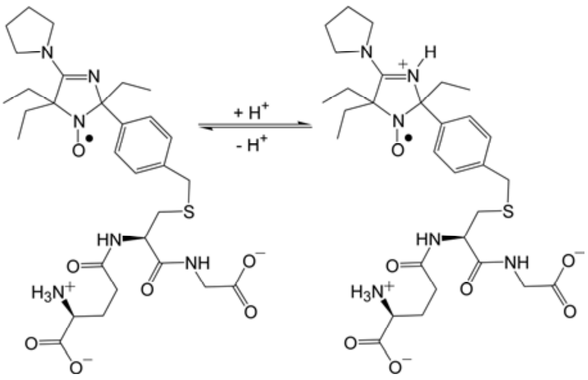

Fig. 1. pH-sensitive nitroxide used in the tumor experiments [2].

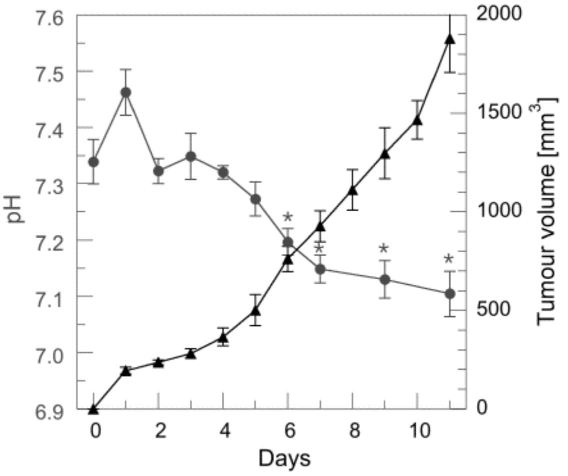

Fig. 2. Relationship between tumor volume (triangles) and pH_e (circles) during normal tumor growth.

This work was supported by grants from Japan Society for the Promotion of Science (NEXT Program LR002 and 26249057 to H.H.) and a grant from NIH (EB014542 to V.V.K.)

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Tue 07 Endogenous iron in rats having amyotrophic lateral sclerosis. An EPR study

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Amyotrophic lateral sclerosis (ALS) is a neurodegenerative disease characterized by progressive degeneration of motor neurons in the primary motor cortex, corticospinal tracts, brainstem and the spinal cord, leading to muscle weakness and atrophy. For years it has been speculated that there is an increase of free brain iron in a number of neurodegenerative disorders. Accordingly, $^{\bullet}$OH radicals, which are generated via Fenton reaction in which poorly liganded ferrous ions reduce the comparatively harmless hydrogen peroxide, are suspected as main culprits responsible for the neuron damage.

Our previous study showed that there is a progressive release of free iron (presumably from ferritin) in ALS patients and that this release is proportional to the severity of the disease [1]. Examination of cerebrospinal fluid (CSF) of control and ALS patients revealed a difference in the amount of free radicals in favor of ALS patients, while difference in the total iron content in the CSF could not be observed. These results indicate that the crucial factor for the free radical formation is not the amount of iron but its form. Likewise, it is indicated that the possible culprits for the increased radical production in the CSF of ALS patients are redox-active iron complexes, which readily generate free radicals [2].

Since the state of endogenous iron of ALS rats has never been investigated, the aim of this study was to use low temperature X-band EPR spectroscopy to investigate the state of Fe in in homogenates of different brain tissues isolated from SOD1^{G93A} transgenic ALS model and age-matched wild type rats. Our data revealed different amounts of Fe in the cortex, hippocampus, brainstem and the spinal cord and several signals in EPR spectra that arise from paramagnetic metalloproteins. The EPR spectrum of the SOD1^{G93A} spinal cord homogenate has an additional signal that was clearly observed at 4K and may be attributed to polynuclear ferric aggregates. The results clearly indicate different metaloprotein composition of homogenates from SOD1^{G93A} compared to wild type rats. Their role in free radical production is under investigation.

This study was supported by the Ministry of Education and Science of the Republic of Serbia (project # III41005).

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Tue 08 Following the reactivity of radicals by time-resolved EPR and CIDNP

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In this presentation, it will be indicated how light-induced reactions of chemically and biologically relevant molecules can be followed by time-resolved EPR (CIDEP). Whereas, it is crucial to observe short-lived radicals at the 50 ns time scale by EPR, it is also important to identify the products formed from these radicals. This can be accomplished by photo CIDNP (chemically-induced dynamic nuclear polarization).

It will be shown how the combination of these two methods leads to an integrated approach for the evaluation of the chemical reactivity of radicals.

Examples from the field of radical polymerization and antioxidants will be given.

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Tue 09 New developments and applications of distance measurements using Gd^{3+} spin labels

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In recent years we have demonstrated the utility of DEER (double electron-electron resonance) distance measurements in proteins spin labeled with Gd^{3+} tags. Such measurements are particularly useful at W- and Q-band frequencies due to the high sensitivity they provide. Here we present further development of this approach. Measurements on a series of bis-Gd^{3+} rigid model compounds with different Gd^{3+}-Gd^{3+} distances that was prepared by Godt and Qi showed that distances as high 8.5 nm can be determined, whereas for distances of 2.5 nm and below the modulations are severely dumped, yielding an artificially broadened distance distribution when using the S=1/2 pair data analysis procedures. In addition, we present measurements on a protein labeled with Gd^{3+} attached to an unnatural amino acid that nicely track conformational changes induced by ligand binding. Finally, we show that owing to the high sensitivity of Gd^{3+}-Gd^{3+} distances measurements at W-band and the stability of Gd^{3+} chelates, in-cell distance measurements are within our reach.

Tue 10 Recent advances in the structural applications of the high-level non-empirical calculations of the NMR parameters

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Dmitry O. Samutsev, Valentin A. Semenov

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Recently, a vast amount of interest has been focused on structural and stereochemical applications of various computational schemes used to calculate second-order molecular properties including basic NMR parameters - chemical shifts and spin-spin coupling constants. Among a variety of theoretical approaches used for this purpose there are two principal groups of methods, namely those based on the Density Functional Theory (DFT) and those stemming from the wave function formalism within the Moller-Plesset Perturbation Theory. Within the latter, two most promising approaches are those based on the Coupled Clusters theory (CC2, EOM-CCSD, CCSD, CCSD(T) and CC3) and, on the other hand, those based on the general Polarization Propagator theory (SOPPA, SOPPA(CC2), SOPPA(CCSD) and, most recently, ADC).

In this laboratory, extensive studies of the stereochemical behavior and stereochemical applications of spin-spin coupling constants of different types including ^{1}H-^{1}H, ^{13}C-^{1}H, ^{13}C-^{13}C, ^{31}P-^{1}H and ^{77}Se-^{1}H were performed in the recent decade within the general Second Order Polarization Propagator Approach family of methods developed by Sauer and coworkers - SOPPA, SOPPA(CC2) and SOPPA(CCSD) in a large number of saturated carbocycles, nitrogen-containing heterocycles, organic phosphines and phosphine chalcogenides, selanylalkenes, five- and six-membered selenium-containing heterocycles, and even in much larger molecular systems like selenosugars. Performed high-level relativistic calculations of ^{77}Se-^{13}C spin-spin coupling constants in the series of selenium heterocycles and their parent open-chain selenides revealed that relativistic effects play an essential role in the selenium-carbon coupling mechanism and could result in a contribution of about 15-20% of the total values of the one-bond coupling constants noticeably improving the agreement of the calculated couplings with experiment. The most remarkable feature of the coupling constants found in all of the mentioned compounds is their marked stereochemical behavior originated in the topology of the coupling pathway and, in particular, that dealing with the spatial orientation of the heteroatomic lone pairs towards the latter.

The second line of our studies is the calculation of magnetic shieldings (chemical shifts) of "heavy nuclei" like ^{29}Si, ^{31}P, ^{77}Se and ^{125}Te to reveal intra- and intermolecular coordination effects at the ZORA-GIAO-DFT level of approximation demonstrating that the contribution of the relativistic spin-orbit interaction mechanism was of crucial importance in the calculation of ^{29}Si, ^{31}P, ^{77}Se and ^{125}Te NMR chemical shifts. Also, it has been found that the main three factors affecting the accuracy and computational cost of the GIAO-DFT calculation of NMR chemical shifts are as follows: the geometrical factor, the most efficient functionals and basis sets and the use of the Locally Dense Basis Set approximation. It has been demonstrated that in the calculation of NMR chemical shifts the best result has been achieved with the KT3 GGA functional of Keal and Toezer in combination with Jensen's pcS-3 basis set (GIAO-DFT-KT3/pcS-3), and this is indeed a very encouraging result for the future studies in this field.

Tue 11 Spin dynamics in frozen solutions of concentrated trityl radicals

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Triaryl methyl free radicals (trityl or TAM) with extremely narrow EPR spectra are used to measure O_2, pH and phosphate concentrations in cells and tissues and to create hyperpolarized nuclei through dynamic nuclear polarization (DNP) for nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) studies. The use of trityls will increase because recent advances in the high-yield synthesis of asymmetric, substituted trityl radicals [1,2] allow design of trityls designed for specific uses.

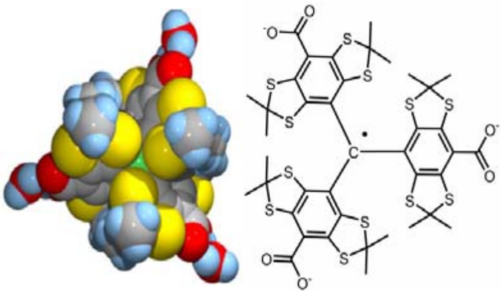

Fig.1. Finland trityl

For DNP, the electron spin polarization of a concentrated frozen solution ($>10^{19}$ cm^{-3}) of trityl radicals is transferred to nuclear spins of other molecules through a series of steps involving electron spin diffusion, cross-relaxation and polarization transfer. At the trityl concentrations used, a substantial number of trityls are in physical contact with each other. The electron spin dynamics responsible for DNP are altered by strong interactions between the trityls. The dynamics producing DNP are very different from those in dilute solution. Optimization of DNP, particularly by design of better trityl radicals requires a fundamental understanding of the spin dynamics at high concentrations and how they depend on molecular properties of the trityl.

We have measured electron spin dynamics of tris(8-carboxyl-2,2,6,6-tetramethylbenzo [1,2-d;4,5-d’] bis [1,3]dithiol-4-yl)methyl, Fig.1, also known as Finland trityl. Spin-lattice relaxation, T_{1e}, has non-exponential kinetics resulting from temperature-independent spin diffusion to fast-relaxing pairs or triads of trityls with an exchange splitting of 15 K. Relaxation, T_{1D}, of the dipolar reservoir that polarizes the nuclei was measured from the Jeener-Broekaert dipolar echo and from the spectral diffusion kernel. T_{1D} depends on trityl concentration but not on temperature with kinetics that follows the Dzheparov theory [3]. The concentration and temperature dependence of T_{1e} and T_{1D} qualitatively explain the efficiency and rate of DNP in low temperature trityl solutions.

Authors are grateful to the Russian Foundation for Basic Research (grants No. 13-04-00680A and No. 11-03-00268) and National Institute of Biomedical Imaging and Bioengineering (NIH, USA, grant No. 5P41EB002034) for financial support.

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Tue 12-1 Solution NMR structures of the Arctic and the wild types of Alzheimer's Aβ peptides in membrane mimicking environment

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The "Arctic" (E22G) single-point mutation of the Alzheimer's Aβ peptide is a rare mutation found in a few families in northern Sweden, leading to earlier onset of Alzheimer's disease [1]. It has been shown that the arctic mutation is one of known intra-β-amyloid mutations causing a typical clinical picture of Alzheimer's disease.

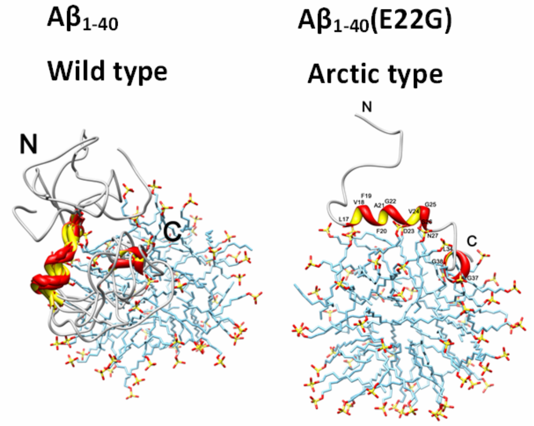

Fig.1. NMR structures of the arctic and the wild type $A\beta_{1\text{–}40}$ bound to a SDS micelle

We used 2D NMR spectroscopy to investigate the conformation of the "wild type" and the "Arctic" mutation of $A\beta_{1\text{-}40}$ Alzheimer's amyloid peptide in a sodium dodecyl sulfate micelle solution mimicking biomembranes [2]. The solution structures revealed that the Arctic mutation of $A\beta_{1\text{-}40}$ interacts with the surface of SDS micelles mainly through the Leu17-Asn27 3_{10}-helical region, while the Ile31-Val40 region is buried in the hydrophobic interior of the micelle. In contrast, the wild-type $A\beta_{1\text{-}40}$ interacts with SDS micelles through the Lys16-Asp23α-helical region and the Gly29-Met35 fragment. Interactions are hydrophobic in nature for both the mutant and the wild-type peptides. These observations clearly show that both the peptide conformation and the peptide-to-membrane binding are very sensitive to a single amino acid substitution, such as E22G in the case of the Arctic mutation. Single amino acid substitutions may affect the rate of aggregation, structure and interaction of toxic oligomers of Aβ peptides with phospholipid membranes that may be correlated with pathogenicity differences of Aβ variants causing early onsets of Alzheimer disease.

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Tue 12-2 Next generation bench top ESR spectrometer with scientific sensitivity

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The MS5000 is a completely new designed EPR spectrometer based on the latest developments in microelectronics, microwave-, and microprocessor technology. It opens new horizons in the combination of performance, usability, and cost effectiveness. It is a compact, cost effective portable bench top system, however, at the same time it provides a true alternative to traditional large scientific EPR systems, particularly in terms of performance features such as sensitivity, great versatility, reliability, user comfort, and easy service.

Mechanical and electronic concept:

- Very compact ruggedized mechanical design. The entire electronics is based on a few tiny high- tech PCB boards including microwave integrated circuits.
- The system employs extensive automatic self- test and calibration facilities
- All accessories such as autosampler, sample cooling or heating systems, goniometer and so on are connected by a proprietary bus system and can be easily attached to the main EPR system at any time

Magnet system:

- Magnetic field range 1 mT to 650 mT
- Magnetic field resolution 0.03 µT (digital resolution 24 bit)
- Magnetic field scan range: any within 1 mT and 650 mT
- Magnetic field scan resolution up to 120,000 steps, scan times of 1 s to 1 h
- The system is completely air cooled, very low noise ventilation

RF System and signal channel

- Fully automated Q factor measurement of resonator
- “DC” EPR measurements without any modulation for measurements on spin systems with extremely long spin lattice relaxation (“rapid passage measurement”)
- Extremely low frequency magnetic field modulation of 5 Hz to 30 Hz for EDMR-measurements
- Transient measurements with time resolution down to 2 µs
- Special “saturation enhanced EPR-measurement” technique with EPR-signal intensities according to the individual saturation behavior of EPR-lines. This greatly helps to identify individual lines in complex EPR-spectra. At a given microwave power and temperature, heavily saturated lines exhibit large signals whereas unsaturated lines do not show up at all.
- Signal channel dynamic better than 130 dB. This enables the detection of extremely weak lines as well as extremely strong lines in the same spectrum. No “amplification factor” or similar needs to be set before the measurement.

Tue 13-1 Verification of MRI-based fiber tracking results

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Magnetic resonance imaging gives a unique possibility to investigate the internal structure of human body in vivo. Measuring the anisotropy of diffusion it is possible to detect local directions of axonal fiber tracts in brain and follow the pathways of axonal fibers. However since the diameter of axons is in the range of a few micrometers, while the linear size of voxel in MRI is by several orders of magnitude larger, the averaging by different fiber tracks within the voxel results in averaged directional information. In regions where several fiber tracks exist in the voxel, tracking can be done in a wrong direction and instead of existing fiber tracts wrong pathways can be found.

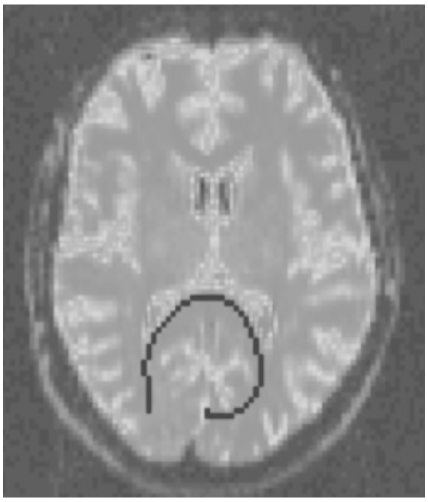

Fig.1. Apparent diffusion map calculated from MRI data measured in healthy volunteer with one of fiber tracts detected in corpus collosium (black line). Fiber tracts in this region are highly parallel. Probability measure calculated along the presented pathway had the lower value (-385 in a.u.), while this measure was higher along tracts with crossing regions or along the wrong way across the existing fiber tracts (-323 in a.u.).

In this work analyzed the main sources of errors in fiber tract detection with different classes of fiber tracking algorithms. Numerical experiments were done on digital phantoms with known pathways of the tracts. Streamline algorithms were more prone to errors in fiber direction caused by noise in data. Even for several parallel fibers bundles were detected "jumps" between neighbor parallel tracks. Global tracking method was more accurate in such case and was better in crossing regions. To characterize the ambiguity detect the particular tract we suggested to use the probability like metrics, modified from probability maps introduced by Koch et al. [1], [2]. Probability measure calculated along the tract presented in Fig.1 was higher that along "wrong" tracts.

This work was supported by RFFI Grant 13-02-00925.

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Tue 13-2 **Towards enhancing oil NMR signal**

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Since middle 1950s, when oils paramagnetism was discovered [1], an attractive opportunity for enhancing oil NMR signal is dynamic nuclear polarization (DNP). Oils contain free radicals in asphaltene complexes, which could be used for DNP. In 1958 a fifteen times enhancement of NMR signal in oil sample was reported [2]. Nevertheless, in later reports asphaltenes in solution were used as a sample for DNP.

DNP could improve sensitivity for NMR relaxometry and porosimetry of fluid-saturated rocks (cores), as well as extracted oil at the wellsite. Core samples contain basically a few percent of fluid, which leads to a small duty ratio and a reception antenna sensitivity loss. Moreover, increasing the sensitivity by increasing of the external magnetic field leads to loss of mobility and increases the cost of the installation and study.

In order to clarify is it possible to use DNP methods to enhance NMR signal in oils we have designed and assembled pulsed NMR spectrometer with DNP. Magnetic field of 10 mT is generated by two Helmholtz coils. They are compact and light compared to iron magnets. For NMR detection we have used 50 ohm coupling scheme, 100 watt transmitter, selective receiving amplifier and Fourier transform. For saturating EPR line we have used homebuilt loop-gap resonator with inductive coupling [3] and 500 watt power amplifier. With 20 watt power transmitted to the resonator we have obtained 2.1 Oe RF magnetic field magnitude, which, according to [2], is enough for optimal DNP. Synchronization and control of all blocks was done by PLIC.

Tests performed with the spectrometer on a chromium complex in ethylene glycol have showed 50 times enhancement of proton NMR signal at 16 watt pumping power, which corresponds to earlier data. Preliminary experiments have shown a weak DNP effect in asphaltenes in solution samples.

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Tue 14-1

Online NMR reaction monitoring in ionic liquids

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The growing interest to reactions in ionic liquids (ILs) is conditioned by their high stability at elevated temperatures, tunable chemical and physical properties. NMR spectroscopy is a powerful tool for online and offline reaction monitoring in ILs in order to perform studies of chemical reactions, extraction, quality control. The number of NMR measurements in ionic liquids rapidly expands. Well-known carbohydrate transformation into 5-hydroxymethylfurfural (5-HMF) is reviewed.

Continuing our study that was started in 2011, we focused on different tasks. Our first step was the identification and quantification of reaction components. We successfully utilized carbon-13 spectra that have wide signal spread and extra loss overlap compared to ^{1}H spectra. After determination of T_1 relaxation times for carbon-13 of ionic liquid media and solutes we optimized experimental conditions. As the mechanism of the conversion of carbohydrates to 5-hydroxymethylfurfural (5-HMF) was studied at the molecular level with the detection of anomers and intermediate species, we continued our studies by investigation of reaction kinetics and further product transformation. The novel Bruker software, Dymanic center was used for these purposes and tested on these objects.

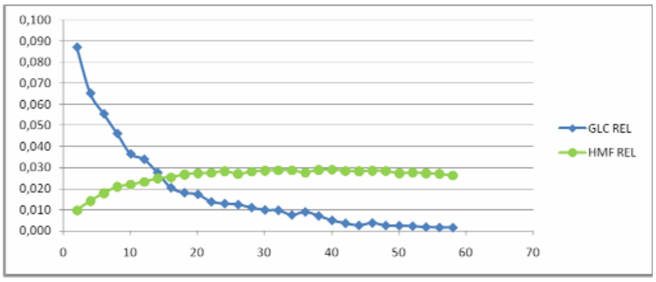

Fig.1. Reaction kinetics for glucose--> 5-HMF transformations calculated by Dynamic Center

Further research was focused on identification of minor compounds and byproducts.

1D and 2D NMR spectra for a broad range of IL systems open possibilities for quantification and this approach was useful for conducting mechanistic studies in native-state ionic liquids. Reaction kinetic studies showed competitive processes of 5-HMF formation and further degradation (Fig.1). Following the analyzed data, it became possible to optimize reaction conditions for maximum yield of target product.

Authors thank Dr. Anna Codina (Bruker UK) for Dynamic Center support and consultations

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Tue 14-2

Application of electron paramagnetic resonance in the investigation of travertine barite

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Structural defects are an essential part of the crystal and are entirely determined by the symmetry elements and translational symmetry of a regular system points [1]. Point defects are formed due to anion and cation vacancies of the crystal structure. The concentration of these defects depends on the conditions of the minerals formation and the dose of natural irradiation. Valence state of the ion radicals may vary and change from diamagnetic to paramagnetic state and vice versa. Impurity ions reflect the chemical environment of minerals and rocks formation. The set of radical EPR spectra were detected for the natural single crystals of barite, the spin Hamiltonian parameters of which [2] were then used for identification of paramagnetic centers in powder [3].

The main goal of this work is to study the formation conditions of barite minerals. Studying of the EPR spectra before and after irradiation and thermochemical treatments of barite minerals was executed on X-band PS-100.X (ADANI, Minsk, Belarus) spectrometer. X-ray analysis of crystal structure was carried out on the SHIMADZU XRD-7000 device.

The objects of the study were barite aggregates forming block- and column-shaped barite buildups up to 10 m high from the Derugin Basin, Sea of Okhotsk [4]. Their formation took place as a result of deep outputs of barium-containing fluids (white smokers) in the near-bottom part of the Okhotsk Sea. Rapid crystallization of barite in unloading areas due to the interaction of Ba^{2+} ions and SO_4^{2-} anions of sea water and the relentless degassing of solutions predetermined formation of so-called porous travertine-like barite aggregates (figure). Radiological assessment of the test sample also showed the association of barite mineralization to elevated contents of ^{226}Ra, ^{232}Th, ^{40}K indicating the enrichment of fluids with radioactive elements. Barite is one of the cheapest protective materials in the construction of "burial" and in nuclear power reactors.

This work was funded by the subsidy of the Russian Government to support the Program of competitive growth of Kazan Federal University among world class academic centers and universities.

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Tue 15-1 Temperature and radiation dynamics of organic matter from electron paramagnetic resonance

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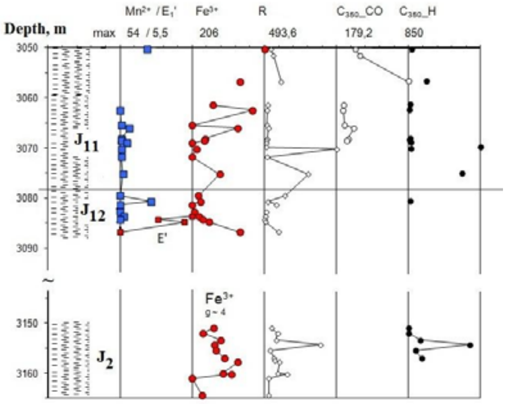
Revealing the conditions and mechanisms of oil pools evolution based on optical and electron microscopy, electron paramagnetic resonance (EPR) is a necessary step to create established improved recovery methods [1]. The features of impurity and host defects of structure minerals rocks and organic matters are reflected in their genetic nature. Distributions of the intensity and lines shape of EPR spectra, and sets of paramagnetic centers across the depth of wells are determined by internal and external conditions of formations of reservoir rocks.

Application of EPR method to study of the temperature, radiation and mechanical dynamics of organic matters (OM) in the reservoir rocks is the subject of the communication. The rocks of wells of the Jurassic sediments of North-West Siberian petroleum basin were used as investigation objects The measurements were performed at room temperature on the X-band spectrometer PS - 100X (ADANI, Minsk, Belarus) with internal standard Al_2O_3: Cr^{3+} permanently installed in the side hole of the resonator. Thermal annealing of samples was carried out in an electric furnace of SUOL type (180V, 95 W, 1200 ^{0}C) using a quartz tube with a hydrogen or carbon monoxide stream to prevent oxidation of annealing products.



The presence of manganese in the upper part of the Jurassic sediments indicates more humid conditions of sedimentation (figure) [2, 3]. The clay minerals and oxides were marked by observing Fe^{3+} ions EPR with g ~ 4.3 and a broad line at g ~ 2.0, respectively. Two types of organic matter were established by thermo-chemical treatment method of reservoir rocks. Sorption properties of the reservoir rocks were identified through the EPR study after X-ray irradiation and mechanical treatments. The results of special optical and electron microscopy, x-ray diffraction studies, macro-structural and textural features of reservoir rocks well correspond to EPR results.

This work was funded by the subsidy of the Russian Government to support the Program of competitive growth of Kazan Federal University among world class academic centers and universities.

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Tue 15-2 Mechanosynthesis of the fluorite-structure fine powders doped with rare-earth ions

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Term “mechanoactivation”designates the processes of changing the energetic state of a material under conditions of delivering the mechanical energy [1]. Doping with rare-earth (RE) ions makes the fluoride host materials useful for various applications, such as lasers, phosphors, scintillators, superionic conductors. Mechanochemical doping is an effective way of obtaining the RE-doped fluorides. However, mechanosynthesis is not the same as crystal growth or solid-state synthesis.

In the present work using the EPR spectroscopy and X-ray diffraction analysis we show that in the course of the mechanochemical doping of MF_2 (M = Ca^{2+},Sr^{2+} and Ba^{2+}) nanopowders with Er^{3+} ions the substitution of the cation sites by Er^{3+}ions occurs. Investigations of the dependences of the EPR spectra intensities on particle size show that the process of mechanochemical doping with Er^{3+} ions proceeds differently for CaF_2, SrF_2 and BaF_2 host matrices. Schematic models of the distribution of the Er^{3+} ions are shown in Fig.1.The data is explained assuming that the result of mechanosynthesis of particles of fluorite-structure fluorides doped with Er^{3+} ions at room temperature is governed by two processes: a) mechanoactivated diffusion of rare earth ions into particles (L_D^{MA}), and b) segregation of the impurity ions to the grain boundaries (L_{seg}).

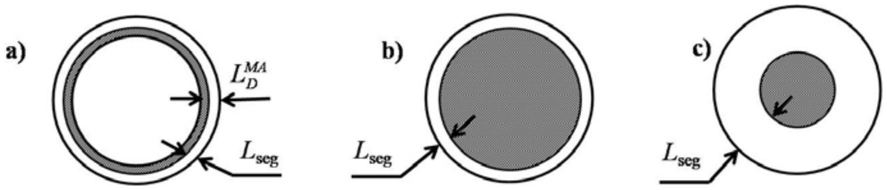

Fig.1. Schematic models of (a) CaF_2:Er^{3+}, (b) SrF_2:Er^{3+}, and (c) BaF_2:Er^{3+} mechanosynthesized particles. Hatched areas indicate localized Er^{3+} ions.

To understand the reason of the broadening of the EPR lines of the Er^{3+} cubic centers compared to MF_2: Er^{3+} single crystal, we’ve studied the annealing of our samples. Using EPR we revealed that after the annealing the width of the EPR lines of all the specimens decreased by 2-3 times. It clearly indicates that the crystal lattice defects formed during the material grinding are healed. We’ve found out also that broadening of the EPR lines of the Er^{3+} cubic centers in mechanochemically doped CaF_2 powder is associated mostly with the disorder in the cation sites, while in the cases of SrF_2 and BaF_2broadening occurs due to the cation vacancies and formation of the trigonal symmetry centers in SrF_2 and BaF_2.

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Tue 16-1

Investigation of a Cu(II)-bis(oxamato) complex by ELDOR detected NMR

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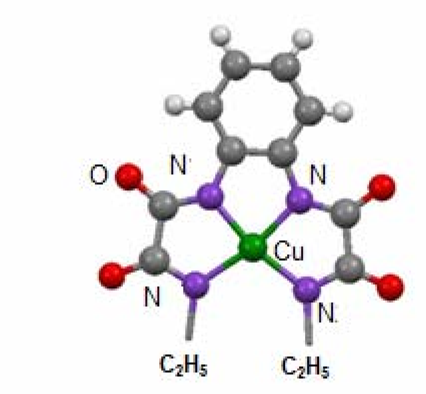
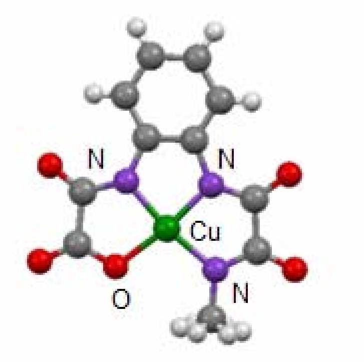
In our previous work, the mononuclear Cu(II)-bis(oxamato) molecular complex with four nitrogen ligands (complex P1, see Fig.) was investigated by pulse ENDOR at the X-band [1,2]. It has been shown that the pulse ENDOR technique could resolve the lines from all four nitrogen nuclei. In this work we present a comparative study of two complexes by the pulse ELDOR detected NMR technique, namely the previously studied complex P1 and the complex P2 with one nitrogen ligand substituted by the oxygen (see Fig.).



P1



P2

We show that pulse ELDOR detected NMR at the Q-band is a very promising method to study such kind of systems. It has enabled us to accurately determine the hyperfine interaction parameters of individual nitrogen ligands. Moreover, despite some disadvantages, this method is less time-consuming and allows to obtain results of a better quality as compared to the X-band ENDOR.

This work has been supported by the Russian Foundation for Basic Research (RFBR grant № 14-02-01194), and by the Deutsche Forschungsgemeinschaft through FOR 1154 “Towards Molecular Spintronics”.

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Tue 16-2

Phase transitions in gypsum products studied by electron paramagnetic resonance

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The products of gypsum annealing are represented by mineral polyphase system in which the co-crystallization and recrystallization processes take place together with the formation of point defects in each of the phase components [1]. Point defects are specific for each component and act as its indicators. Paramagnetic centers in single crystals of natural anhydrite were studied in [2].

X-ray activation of paramagnetic centers in gypsum single crystals («Marino steklo») was used to identify and define the parameters of spin Hamiltonian of SO_4^--H; SO_3^-; SO_3^--H; SO_2^- paramagnetic centers [3]. The temperature range of α- and β-phase states of bassanite and γ-anhydrite formation in the process of gypsum dehydration were established by EPR spectra of paramagnetic centers in [3].

The formation of these five phases in the $CaSO_4$-H_2O system and their transformations were investigated by in situ time-resolved synchrotron radiation powder X-ray diffraction (SR-PXD) in [4].

The object of present communication is “technogenic” gypsum which was crystallized in a tube with formation of water as “useless” product. This gypsum was used as a natural model or as a marker of arid crystallization conditions. The aim of this research was to determine the effect of gypsum crystallization conditions on the properties of gypsum dehydration. For this reason its morphology, paramagnetic centers after X-rays irradiation, and formation of five phases in the $CaSO_4$-H_2O system were studied. Atomic hydrogen EPR spectra were recorded in different phases of gypsum dehydration after X-ray irradiation. A preferential formation of five phases of dehydration gypsum were defined in temperature range from room temperature to 600 ^{0}C.

The EPR spectra were recorded on an X-band PS-100X spectrometer (ADANI, Minsk, Belarus) at 25°C. The intensities of the ESR spectra were compared using a reference spectrum of an Al_2O_3: Cr^{3+} sample inserted into the cavity through a lateral hole.

This work was funded by the subsidy of the Russian Government to support the Program of competitive growth of Kazan Federal University among world class academic centers and universities.

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Tue 17-2 Some applications of NMR for research core and drilling wells.

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The main applications of NMR in the well logging industry include laboratory analysis of rock samples, drilling cuttings and their reservoir properties and the studies of nuclear magnetic properties of the formation fluids in a well.

Well logging started with the wide use of tools in low field modification. In the Republic of Tatarstan low field NMR saw wide application in early 80`s and was included into a standard set of LWD procedures. At present, TNG-Group is the only company that offers low field NMR services and possesses a family of tools with different diameter which enables to carry out measurements in complex wells, including those in new regions.

At present, Russian market of geophysical services experiences greater development of the high field NMR. Currently there are similar downhole tools (MRIL, MREX, CMR, NMTL) based on the application of permanent magnets to create a magnetic field. Under federal project with the Ministry of Education of Russian Federation, TNG-Group along with the Kazan Federal University participated in development of the newest high-tech products. This cooperation has resulted in development of the following tools: downhole MR-imager (MRLT) with dipole magnet; NML-1 high field NMR tool with opposite positioned magnets; NML-2 high field NMR tool built on the application of cryotechnologies to increase depth of investigation and improve sensibility; NMR-Core high field unit for laboratory analysis of large core samples; NMR-Core high field mobile unit for full-size core analysis at the well site.

The model of MR-imager (MRLT) was designed by TNG-Group and tested in the well. The model of NML1 tool was prepared for downhole testing.

NMR-Core unit was designed in laboratory and mobile modifications. Laboratory version of NMR-Core unit employs closed-loop superconducting magnet system to ensure high sensibility. The magnetic field strength makes up 1.5 T which corresponds to 64 MHz proton resonance frequency. Thus, such magnet system is the most optimal for analyzing full-size core samples up to 10 cm in diameter.

All required batteries and electronic units of mobile NML-Core are contained within single case. In addition, the tool is equipped with the sample positioning system that enables to conduct scanning NMR properties of the sample along its length in automatic mode. The unit has been tested at the well site where the core samples were extracted using the isolated technology (in fiberglass pipe). The intervals with movable fluid were identified by the long components of the relaxation times and confirmed by other logging procedures.

Wed 01 Advanced magnetic resonance studies of nanostructured materials and signal enhancement

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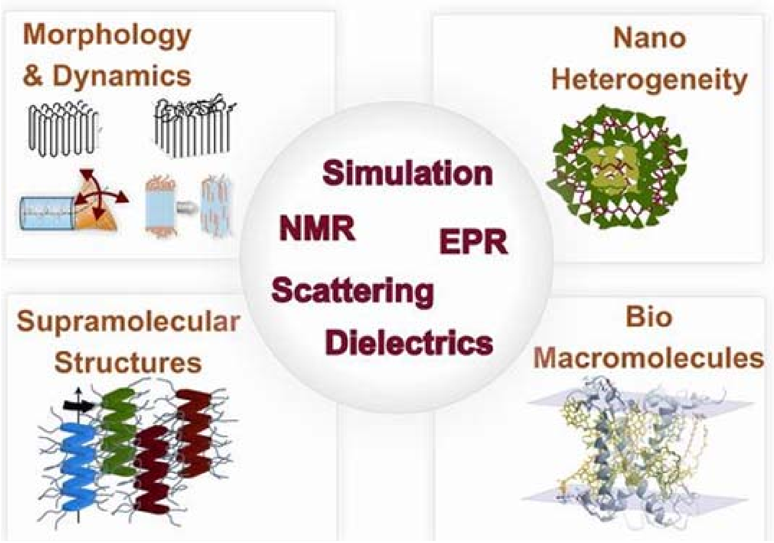
Functional nanostructures are in the focus of current soft matter science. They occur in advanced synthetic as well as in biological systems through self-assembly of carefully chosen building blocks. Secondary interactions such as hydrogen bonding, aromatic pi-interactions, and electrostatic forces are of central importance. Here, NMR spectroscopy provides unique and highly selective information on structure and dynamics [1] of such systems, e.g., on hydrogen bond networks in the solid state, stacking, and cooperative molecular motions of discotics [2], pi-conjugated polymers [3, 4], metal organic frameworks [5], and macrocycles [6]. Moreover, pulsed EPR spectroscopy provides unique information about partially disordered proteins [7].



For full structural and dynamic elucidation, the spectroscopic data have to be combined with other techniques, in particular X-ray scattering, microscopy, dielectrics and last, but not least, quantum chemical calculations [8], as shown in the Figure. Recent examples will be presented and the findings will be related to the function of such materials, such as conductivity.

A major drawback of NMR is its inherently low sensitivity. This can be overcome by hyperpolarization, which can be achieved several ways. I will in particular speak about Para Hydrogen Induced Polarization (PHIP), a chemical method, which makes use of the correlation between nuclear spins in Para-hydrogen to create long-lived hyperpolarized states in organic molecules [9].

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Wed 02 Direct determination of exchange parameters in spin-1/2 Heisenberg triangular-lattice antiferromagnets: high-field ESR studies

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Spin-1/2 Heisenbergantiferromagnets Cs_2CuCl_4 and Cs_2CuBr_4 with distorted triangular-lattice structures are studied by means of electron spin resonance spectroscopy in magnetic fields up to the saturation field and above. In the magnetically saturated spin polarized phase, quantum fluctuations are fully suppressed, and the spin dynamics is defined by ordinary magnons. This allows us to accurately describe the magnetic excitation spectra in both materials and, using the harmonic spin-wave theory, to determine their exchange parameters. The proposed approach has a broader impact and can be potentially used for any quantum magnet with reduced (e.g., by the staggered DM interaction) translational symmetry, resulting, as predicted, in emergence of a new exchange mode in the magnetically saturated phase.

*Published in: S.A. Zvyagin, D. Kamenskyi, M. Ozerov, J. Wosnitza, M. Ikeda, T. Fujita, M. Hagiwara, A.I. Smirnov, T.A. Soldatov, A.Ya. Shapiro, J. Krzystek, R. Hu, H. Ryu, C. Petrovic, and M.E. Zhitomirsky, Phys. Rev. Lett. **112**, 077206 (2014).

Wed 03 Developments and applications of multi-extreme THz ESR

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Recent developments and applications of our multi-extreme THz ESR will be presented. Our system has following specifications and we can combine them to achieve the multi-extreme.

1) Wide frequency region between 0.03 to 7 THz using Gunn oscillators, BWO and FIR laser [1].
2) Magnetic field up to 55 T using the pulsed magnet [1,2].
3) High pressure up to 2.7 GPa using the hybrid type pressure cell [3].
4) Micro-cantilever ESR which enables the detection of micrometer size crystal [4].
5) Magnetization detected ESR using SQUID magnetometer (SQUID ESR) [5].

Application to kagome lattice magnet $[Cu_3(CO_3)_2(bpe)_3]_2ClO_4$ will be shown.

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Wed 04 Novel magnetic resonance technique to detect magnetoelectric coupling in multiferroic materials

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Magnetoelectric (ME) materials exhibiting coupled and microscopically coexisting magnetic and electric polarizations have attracted considerable interest in recent years. In order to detect the ME effect, sensitive and reliable experimental techniques are required, since this coupling is generally quite small. Recently we developed a novel microscopic method for the direct determination of the ME effect based on the standard Ferromagnetic/Electron Paramagnetic Resonance (FMR/EPR) technique combined with electric field modulation [1]. This method is based on the use of electric field modulation instead of conventional magnetic field modulation in standard continuous wave EPR spectrometer.

Application of this method is demonstrated in single-crystal Cu_2OSeO_3, where the ME coupling on spin-wave resonances was studied [1]. The linear ME coupling strength was determined quantitatively. The temperature dependence of the ME coupling was found to follow nearly that of the spin susceptibility without a sudden change across magnetic order temperature. New results obtained in multiferroic thin film oxides will be also presented. Obtained results demonstrate that the novel microscopic technique using FMR/EPR combined with electric field modulation is a very sensitive and powerful tool to investigate the ME effect and to search for new ME materials.

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Wed 05 EPR - a key technique to understand metal biocatalysis

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The investigation of metalloproteins, which are often paramagnetic, is a central field of application for advanced EPR techniques. Metal centers are involved in such interesting processes as catalytic water oxidation, dihydrogen production from protons and the conversion of molecular nitrogen to ammonia. In this contribution the enzymes wateroxidase and hydrogenase are discussed as examples.

Light-induced water splitting and oxygen release ($2H_2O \rightarrow 4H^+ + 4e^- + O_2\uparrow$) is performed by an oxygen-bridged tetranuclear manganese/calcium cluster located in photosystem (PS) II of all organisms performing oxygenic photosynthesis. An energy-minimized structural model of the cluster has been obtained by DFT [1,2] based on X-ray crystallographic data of PS II single crystals [3]. Details of the cluster's electronic structure in its various states of the enzymatic cycle are available from cw/pulse EPR and double resonance technique like ^{55}Mn ENDOR [4,5]. ELDOR-detected NMR (EDNMR) has been used to detect the binding of the substrate water ($H_2{}^{17}O$) to the Mn_4O_5Ca cluster [6]. Based on these data and together with theoretical approaches and additional experiments a robust model for the cluster in its catalytic cycle and the binding of the two substrate water molecules could be obtained, from which – together with theoretical approaches – a mechanism of water oxidation and oxygen release has been developed [7].

Reversible H_2 conversion in Nature is performed by the enzymes [NiFe] and [FeFe] hydrogenase. They contain bridged binuclear transition metal cores in their active sites, which are tuned by a special ligand environment to convert molecular hydrogen to protons or *vice versa* via a heterolytic splitting mechanism ($H_2 \rightleftharpoons H^- + H^+ \rightleftharpoons 2H^+ + 2e^-$). The various intermediate states in the catalytic cycle are studied by spectroscopic techniques; here results from advanced EPR methods are presented [8,9]. The activation of the enzyme, the inhibition by CO, the sensitivity to molecular oxygen as well as substrate binding and product formation have been investigated for both classes of enzymes. This led to proposals for the catalytic cycles of the [NiFe] and the [FeFe] hydrogenases, which have been discussed in a recent review [9].

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Wed 06 Advanced EPR on biomolecules - crossing the gap to NMR

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In this lecture on advanced EPR spectroscopy, considerable emphasis will be put on delineating the complementarity of NMR and EPR concerning the measurement of molecular interactions in large biomolecules. From these interactions, detailed information can be revealed on structure and dynamics of macromolecules that are embedded in frozen-solution environments.

Recent developments in mm pulsed microwave and sweepable cryomagnet technology as well as ultrafast electronics for signal data handling and processing have pushed to new horizons the limits of EPR spectroscopy and its multifrequency extensions concerning the sensitivity of detection, the selectivity with respect to interactions, and the resolution in frequency and time domains. One of the most important advances has been the extension of EPR spectroscopy to high magnetic fields and microwave frequencies, very much in analogy to what happens in NMR. Signal and resolution enhancements are particularly spectacular for electron-nuclear and electron-electron double-resonance techniques such as ENDOR, EDNMR and PELDOR at high magnetic fields. They provide greatly improved orientational selection for disordered samples that approaches single-crystal resolution at canonical g-tensor orientations – even for molecules with small g-anisotropies. Dramatically improved EPR detection sensitivity could be achieved for short-lived paramagnetic reaction intermediates. Unique structural and dynamic information is thus revealed that can hardly be obtained by other analytical techniques. Micromolar quantities of sample molecules have become sufficient to characterize stable and transient reaction intermediates of complex molecular systems – offering highly interesting applications for chemists, biochemists and molecular biologists.

Representative examples of advanced EPR spectroscopy will be reported on such as high-field PELDOR and ENDOR structure determination of cation-anion radical-pair intermediates in reaction centers from photosynthetic organisms; high-field EPR and EDNMR on nitroxide spin-labelled proteins and model systems

Wed 07

Bioinformatics and NMR spectroscopy

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Nuclear magnetic resonance (NMR) spectra at high resonance frequencies give a huge amount of information on a metabolic condition of an organism in the form of metabolic profiles. The most important applications of the analysis of metabolic profiles are the pharmacokinetics, toxicology, the medical diagnostics, demanding big data bases on biological samples. As the NMR spectroscopy allows one to obtain data on a large number of metabolites, the directions connected with the analysis of mutual correlations between metabolites are most fruitful. For creation of successful appendices on the basis of the analysis of metabolic profiles important value has the statistical analysis of obtained data. It is due to the fact that low-molecular biomarkers, as a rule, poorly selective. Usually at initial data processing, for example, at model research of renovascular hypertension on laboratory rats, the methods from area of digital processing of signals are used. The following stage is given by methods without supervision (principal component analysis, methods of the cluster analysis) in order to establish existence of any connections in initial structure of data and to eliminate deviations. Further, depending on a task, the methods of the hierarchical analysis or the methods of the regression analysis of multidimensional data are used. Both approaches is widely used in bioinformatics. The choice of basis is made so that most effectively to carry out regression on available data on samples. Data source of comparison and the data included in the statistical analysis, are the results received by means of various physical and chemical methods (NMR spectroscopy, chromatography-mass spectrometry, infrared and Raman spectroscopy). Interpretation of obtained data on a metabolism and results of classification of samples needs biological, medical and biochemical data. Analysis of the data obtained by means of analytical chemistry and biological data would be impossible without use of different bio - and chemometrix information. Such association, despite lower sensitivity of spectroscopy of a nuclear magnetic resonance in comparison, for example, with chromato-mass spectrometry, allows to realize the advantages of NMR spectroscopy as not selective structural method in biochemical researches.

Thu 01 ESR on correlated ferromagnetic metals

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The presence of a well defined electron spin resonance (ESR) in the heavy fermion metal $YbRh_2Si_2$ well below the 4*f* single-ion Kondo temperature sparked considerable interest in new experimental and theoretical studies. These studies revealed further examples of well resolved ESR lines not only in Kondo lattice systems, but also in 3*d* intermetallic compounds close to a ferromagnetic critical point. The results suggest that the Kondo interaction and the ferromagnetic correlations are important ingredients for the observability of an ESR line in $YbRh_2Si_2$. We shall report our ESR studies on the dense ferromagnetic 3*d*- and 4*f*-based metals, $NbFe_2$ [1] and $Yb(Rh_{0.73}Co_{0.27})_2Si_2$ [2]. For $NbFe_2$ a spin resonance of conduction electrons is observed being determined by details of its electronic band structure. In case of Fe-rich $NbFe_2$ below $T = 30$ K the formation of a spin-density wave type magnetic ordering and, below 22 K, ferromagnetic ordering leads to pronounced splittings of the resonance [3]. For $Yb(Rh_{0.73}Co_{0.27})_2Si_2$ strongly anisotropic spectra indicate a local resonance of Yb-4*f* spins which splits into two lines below the magnetic ordering temperature of 1.3 K. Such a behavior can be explained by the strong anisotropy of the ferromagnetic ground state in agreement with magnetization measurements [2].

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Thu 02 Spin-dynamics in magnetic multilayers by FMR investigations

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Thin magnetic multilayered structures have been studied by Ferromagnetic Resonance (FMR) technique. We used conventional sputtering technique to prepare ultrathin magnetic layers separated by non-magnetic thin metallic layers in order to allow indirect exchange coupling between neighbouring magnetic layers through the non-magnetic spacer. The FMR signal have been recorded by using conventional X-band ESR spectrometer operating at 9.5 GHz microwave frequency. A sample was rotated by a goniometer in a continuous helium gas flow cryostat with respect to external DC magnetic field in order to observe both temperature and angular dependence of FMR signal.

A number of resonance peaks in FMR spectra have been observed. This number depends on the number of the magnetic layers in the structure. That is, the number of peaks increases while their intensities decrease with the number of modes. The separation of the modes in magnetic field decreases with the number of layers as well. However, this separation shows oscillatory behaviour with the spacer thickness.

In order to study the magnetic properties more deeply, we have proposed a theoretical model. A computer programme has been developed to model the experimental data. The programme allows to use different magnetic parameters for different magnetic layers. Thus FMR data have been analyzed to extract magnetic parameters.

It has been found that the thin magnetic layers are indirectly exchange coupled over non-magnetic layers. The saturation magnetization of each individual layer precesses about its own effective magnetic field originating from external DC field and anisotropy field. The interface or surface anisotropy causes a spin pinning at the surface. Thus so-called macroscopic spin waves can be excited. The FMR spectra can include both bulk and/or surface spin-wave modes. In addition to acoustical modes, optical modes can also be excited when the exchange coupling parameter between neighbouring magnetic layers is antiferromagnetic in character.

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Thu 03 Magnetic resonance in spin-gap magnets.

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Various spin-liquid systems are actively studied during the last decades. These systems remain disordered despite of the strong exchange coupling present down to the temperatures well below the Curie-Weiss temperature. This unusual behavior is due to the specific geometry of the exchange bonds usually invoking low-dimensionality, frustration or dimer motives in the spin subsystem. Spin-gap magnets are one of the examples of this kind of spin systems. Spin-gap magnets have a nonmagnetic singlet ground state separated from the magnetic triplet excitations by an energy gap of the exchange origin. At low temperatures the population of magnetic excitations is depleted and magnetic excitations can be considered as a gas of weakly interacting S=1 quasiparticles. Spectral properties of these triplets, their interaction and relaxation can be studied in details using the electron spin resonance (ESR) technique. Another interesting question is a stability of the singlet ground sate against the applied magnetic field or against a disorder. Here, again, the high spectral resolution of the ESR spectroscopy allows to obtain new results that compliments essentially other experimental techniques.

We will discuss two recently studied spin-gap magnets: (i) a two-dimensional spin-gap magnet $(C_4H_{12}N_2)Cu_2Cl_6$ (abbreviated as PHCC) which provides an opportunity to study effect of exchange bond disorder by substituting part of the bridging Cl ions by Br, and (ii) an one-dimensional spin-ladder $(C_7H_{10}N_2)_2CuBr_4$ (abbreviated as DIMPY) which turned out to be almost perfect Heisenberg model.

Pure PHCC is a 2D spin-gap magnet with the dimer motives in the exchange bonds network. Its spectral properties were studied in details earlier, including ESR study of the present authors [1]. This makes it a convenient target to study the effect of bond-disorder on the spectral properties of a spin-gap magnet. This disorder can be introduced in a controlled way by substitution of the bridging Cl ions by Br. We observe broadening of the ESR line with doping indicating shortening of the quasiparticles lifetime. We have found that at low temperatures ESR response of the highly doped samples is governed by S=1 centers which are most likely ferromagnetically coupled pairs of S=1/2 Cu^{2+} ions. Evolution of the ESR absorption from high-temperature single-component line to the absorption spectrum of the S=1 triplet excitations split by an effective crystal field at intermediate temperatures and to the response of a paramagnetic S=1 spin-pairs at the lowest temperatures can be followed [2].
DIMPY is a rare example of the strong-leg spin ladder [3]. Absence of the zero-field splitting of the triplet sublevels indicates that anisotropic interactions are really weak in this system. Structure of DIMPY includes two magnetically inequivalent ladders (related by a C_2 transformation). ESR spectra allow to resolve signals from these ladders, indicating that the ladders coupling is also negligible. Thus, DIMPY is very close to the ideal Heisenberg model. The temperature dependence of the ESR linewidth in DIMPY demonstrates several maxima indicating switching between different relaxation mechanisms.

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Thu 04 Revealing the local magnetism of S=1/2 Kagomé lattice $ZnCu_3(OH)_6Cl_2$ using single crystal NMR

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Herbersmithite $ZnCu_3(OH)_6Cl_2$ is known to be a promising candidate material hosting a quantum spin liquid ground state. The recent success in single crystal growth of $ZnCu_3(OH)_6Cl_2$ as well as the discovery of a continuum of spin on excitations using inelastic neutron scattering [1] have opened a new chapter in the study of highly frustrated magnetism.

However, the mechanism behind the realization of the non-magnetic ground state in $ZnCu_3(OH)_6Cl_2$ remains controversial, mainly due to the difficulty in understanding the role of defects in its physical properties. To distinguish the intrinsic magnetism of the kagomé lattice from the defect contribution, we used ^{17}O, ^{63}Cu, ^{2}D, and ^{35}Cl NMR to probe the local behavior of spin susceptibility and spin dynamics, which provided invaluable insights into the nature of defects and their potential influence on the kagomé spin lattice [2].

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Thu 05

Nuclear polarization in silicon in high magnetic fields and low temperatures

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Shallow donors in silicon (P, Bi, As) attract extensive research efforts due to a possibility of building a quantum computer where the donor nuclear spin is used as a qubit, and the electron spin provides means of the qubit control and readout [1]. Dynamic Nuclear Polarization (DNP), an old and well-known tool for the nuclear spin control and manipulation, may be effectively used for practical realization of this idea. In this work we report on experimental studies of dynamic nuclear polarization (DNP) and relaxation of ^{31}P donors and ^{29}Si in natural (4.6% of ^{29}Si, spin 1/2) silicon. For the first time such study is performed in a strong magnetic field of 4.6 T and temperatures below 1 K, when the donor electron spins are fully polarized and the relaxation times of electrons and nuclei are very long. We used continuous wave 130 GHz electron spin resonance (ESR) for diagnostics and manipulation of the electron and nuclear spins.

We utilized Overhauser effect for DNP of ^{31}P. The inhomogeneously broadened ^{31}P ESR lines of about 4 G in width were pumped with a frequency modulated ESR excitation, effectively covering the whole line. Pumping the high field line with very low RF powers (<1 μW) created a DNP of ^{31}P exceeding 98% in 20 minutes. Pumping the low field line with the same excitation, however, polarized the ^{29}Si nuclei interacting with the ^{31}P donors. We demonstrate that by adjusting the pumping conditions, we were able to reach high DNP values of ^{29}Si for nearly throughout the sample. Pumping without the modulation creates a narrow spectral hole owing to a DNP of the nearby ^{29}Si interacting with the donors.

We also realized DNP of ^{29}Si via the resolved solid effect by pumping the ^{31}P-^{29}Si forbidden electron-nuclear transitions. As a result we observed a pattern of narrow holes and peaks in the ESR spectrum, corresponding to polarization of ^{29}Si in the specific lattice sites, resolved by the strength of the superhyperfine interactions, around the donors. This opens a way for creating entangled states of ^{29}Si spins, and realization of quantum operations with large ensembles of identical nuclei.

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Thu 06

NMR-paradigm pulse ESR spectroscopy: Coherent multi-frequency spin manipulation technology for spin-based quantum computers and quantum information processing

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Considerable research on quantum computing and quantum information processing (QC/QIP) has been achieved from the theoretical side for the last decades. Among physically realized qubits, molecular electron spin qubits have been the latest arrival [1-4], although electron spins in molecular frames have naturally been anticipated as typical matter spin qubits. In quest of ensemble molecular spin qubits from the chemistry and materials science sides, "a" smallest QC has been implemented, in which controlled-NOT gates are for the first time established [4]. Among the essential issues relevant to QC/QIP, all the physical qubits have faced the issues of qubit scalability and quantum error corrections associated with decoherency of qubits. The solution-NMR approach has brought QC down to earth in terms of spin qubit manipulation technology, but suffers from the lack of real entanglement [1,3]. In this context and molecular optimisation, electron spin qubits are promising because they maintain intrinsic high polarization and play a hyperpolarizing role in molecular quantum spin cybernetics.

From the viewpoint of quantum cybernetics, we survey so far established electron/nuclear spin manipulation technology for ensemble molecular spin qubits, in which the electron and nuclear spins play a bus qubit and client ones, respectively [1-4]. By invoking electron-nuclear coherency established in a molecular system we have for the first time shown the experimental evidence of the electron spinor [2]. In terms of pulse-based microwave spin resonance techniques, the number of available coherent multi-frequencies has been limited and thus far molecular spin qubits haven't afforded their advantages in the field of QC/QIP. Recent theoretical progress in QC/QIP and quantum cybernetics requires coherent control of multi-frequency electron spin qubits in ensemble, in which electron and spin qubits are equivalently manipulated in a desired manner. Recently, we have established the electron spin manipulation technology with arbitrary wave generators (AWGs), which is based on coherent microwave pulsed multi-frequency resonance techniques for the precise manipulation of molecular spins. This new technology with the AWG apparatus is underlain by the paradigm of NMR spectroscopy and can widely be applicable to various types of pulsed ESR experiments including coherent electron-spin multiple resonance in chemistry, physics, materials science and their related fields.

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Thu 07 Non-Traditional Approach to Quantum Computing

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The spinor representation is traditionally used for quantum information applications connected with liquid state NMR, solid state NMR/EPR, quantum dots, endohedral fullerenes, nitrogen-vacancy centers in diamond, ^{31}P centers in silicon, rare-earth ions, single molecule magnets, Josephson contacts and others. Fundamental quantum gates, quantum algorithms, quantum error corrections and issues in quantum information theory have been demonstrated at the level of a few qubits using liquid state NMR systems at room temperature. NMR is attractive as a candidate for quantum computing because of long coherence time exhibited by the spins and also due to complexity of logical operations that can be executed on modern NMR spectrometers [1].

We consider a system of N spins with a 2^N-dimensional Hilbert space. The state of N qubits can in general be represented by a 2^N-dimensional complex vector. On the other hand, the set of N qubits satisfies the relationship $I = 2^{N-1} - 1/2$, where I is the effective spin corresponding to N qubits related to a systems of nuclear or electron spins.

Any state of N qubit quantum computer can be presented as a linear superposition of the $2I+1$ products of Bose states $|2I\rangle_1|0\rangle_2, |2I-1\rangle_1|1\rangle_2, ..., |1\rangle_1|2I-1\rangle_2$, and $|0\rangle_1|2I\rangle_2$ as follows:

$$\Psi = \sum_{m=-I}^{I} C_m |I+m\rangle_1 |I-m\rangle_2 , \tag{1}$$

where the coefficients satisfy the normalization condition $\sum_{m=-I}^{I} |C_m|^2 = 1$.

The ket-vectors $|I+m\rangle_1$ and $|I-m\rangle_2$ are the states of two non-interacting Bose fields that are correlating between themselves. Between creation and destruction operators of these fields the relationship $a_1^+ a_1 + a_2^+ a_2 = 2I$ takes place. This formula takes into consideration Bose states that does not participate in realization of two-Bose operators representation of the spin momentum by means of unitary spinor operators U and U^+, where

$$U^+ = \left(\frac{1}{\sqrt{(2I)!}} \left(a_1^+\right)^{2I} \quad \frac{1}{\sqrt{(2I-1)!}} \left(a_1^+\right)^{2I-1} a_2^+ \quad ... \quad \frac{1}{\sqrt{(I+m)!(I-m)!}} \left(a_1^+\right)^{I+m} \left(a_2^+\right)^{I-m} \quad ... \quad \frac{1}{\sqrt{(2I-1)!}} a_1^+ \left(a_2^+\right)^{2I-1} \quad \frac{1}{\sqrt{(2I)!}} \left(a_2^+\right)^{2I} \right).$$

The presentation of the wave function of a N-qubit quantum computer in the form (1) is due to the invariance of the spin projection operators under orthogonal addition and orthogonal reduction of the spinor basis vectors. As a consequence of this invariance, the operators $I_\pm = I_x \pm iI_y$ and I_z are $I_+ = a_1^+ a_2$, $I_- = a_2^+ a_1$ and $I_z = (a_1^+ a_1 - a_2^+ a_2)/2$ independent of the spin value. These operators are simple quadratic forms for any values N of number of qubits that must be used successfully in quantum computing (evolution operators, spin-dependent density operators, the gate operations NOT, **Y**, **Z**, Hadamard, phase gate and others). Particularly, the Hadamard gate for a N-qubit quantum computer is

$$\mathbf{H}_N = \frac{1}{2^{N/2}} \left[a_1^+ (a_1 + a_2) + (a_1 - a_2) \right] \otimes \left[a_1^+ (a_1 + a_2) + (a_1 - a_2) \right] \otimes ... \otimes \left[a_1^+ (a_1 + a_2) + (a_1 - a_2) \right],$$

where the sign of the Kronecker product $\otimes$ is used $N-1$ times.

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Thu 08-1

Multiple quantum NMR in one-dimensional and nanoscale systems: theory and computer simulations

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Multiple quantum (MQ) NMR spectroscopy [1] is a powerful tool to study the nuclear spin distributions in different systems (liquid crystals, simple organic systems, amorphous hydrogenated silicon, etc.), investigate the size of spin clusters when their growth occurs in the process of the irradiation of the spin system on the preparation period of the MQ NMR experiment [1], and study the decoherence rate for highly correlated spin states.

The dependence of the intensities of MQ NMR coherences on their orders (the profile of MQ NMR coherences) is an important characteristic of the above classes of systems because it contains a wealth of physical-chemical information. A simple combinatorial model [1] predicts a Gaussian profile of MQ NMR coherences. This conclusion was confirmed qualitatively in some experiments [1]. Since the model is based on very rough assumptions, one can expect discrepancies with experimental data in some cases. Numerous experimental data were investigated in Ref.[2] and the authors found that the profiles of the MQ NMR intensities are rather exponential than Gaussian.

Our main goal is to create a full quantum-mechanical theory which would explain the observed profiles of the intensities of MQ NMR coherences. Presently, this problem cannot be solved for arbitrary three-dimensional spin systems. Thus, as a first step, we considered one-dimensional systems. We introduced a model of an isolated spin chain and showed that the MQ NMR Hamiltonian of such a system is an XY Hamiltonian which can be diagonalized exactly in the approximation of the nearest neighbor interactions [3]. Eventually, we have found [3] that only intensities of MQ NMR coherences of the zeroth and +/- second orders are nonzero. It means that this model does not yield a solution to the problem. The situation does not change when we consider MQ NMR dynamics of one- dimensional systems at low temperatures and even in alternating spin chains in the approximation of the nearest neighbor interactions.

Next, we considered nanopore materials whose nanopores are filled with spin-carrying atoms (molecules). Since molecular spin diffusion is faster than spin flip-flop processes, one can average the dipole-dipole interactions (DDI) over molecular diffusion. Then the DDI coupling constants are the same for all spin pairs and we can investigate the MQ NMR dynamics in systems with several hundred spins [4]. Our numerical analysis showed that the profile of the intensities of the MQ NMR coherences is exponential in agreement with the experimental data [2].

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Thu 08-2 Magnetic structure of $CuCrO_2$ according to copper NMR

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Cu NMR spectra in single crystal of a triangular-lattice antiferromagnet $CuCrO_2$ in magnetic field μ_0H up to 15.5 T applied perpendicular and parallel to the *c*-axis of the crystal have been investigated.

The shapes of the spectra at temperatures below the ordering temperature $T_N \approx 24$ K are strongly dependent on the field direction and cooling history of the sample. The spectra were studied under two cooling conditions: zero field cooling and field cooling. Example of zero field cooling spectra when the static field is oriented in *ab*-plane is shown in Fig.1. The angles correspond to the directions of the external field with respect to the [110] direction of the sample. The spectra measured at H||*c* are ~3 times broader than those with H||*ab*-plane, Fig.2. The shape of the spectra depends on the field value. At low field range (μ_0H < ~11 T) the shape has two horns similar to those observed for H||*ab*-plane. For higher fields, an additional third peak appears in the middle of the spectra.

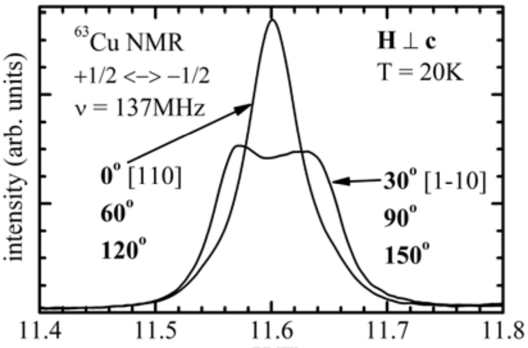

Fig.1

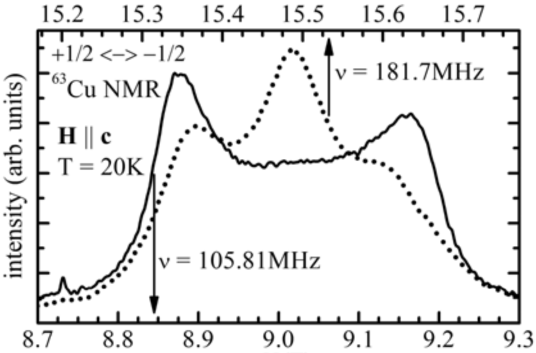

Fig.2

The results are discussed in the framework of planar magnetic structure proposed by neutron diffraction experiments [1]. The data for perpendicular orientation assume remarkable reorientation of spin plane simultaneous with rotation of the incommensurate wavevector influenced by the external magnetic field. These results are consistent with ESR experiments [2]. Parallel field data for the fields higher ~11 T indicate field evolution of the magnetic structure. We suggest two possible models. The first one is incommensurate spiral magnetic structure within every *ab*-plane with disorder in the *c* direction. The second model is commensurate magnetic structure. The observed feature possibly corresponds to a phase transition also seen by recent electric polarization experiments [3].

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Thu 09-1 High-frequency EPR and ENDOR spectroscopy on nanostructures

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Magnetic resonance methods are the basic techniques for studying spin phenomena in condensed matter and biological systems. Spin phenomena are playing a crucial role in the development of devices based on nanostructures. Nanoparticles are also widely used in cell biology and medicine, for transfection, gene silencing, photodynamic therapy, drug delivery, etc.

Since 2007 in the EPR division of the Centre of the Shared Facilities of Kazan Federal University we investigate special nanostructures. By means of multifrequency EPR and ENDOR we investigate quantum confinement of electron wave function in doped nano – ZnO quantum dots [1-4]. Our interest to the nanohydroxyapatite (nano-HAp) study was initially governed by a search for reliable prognostic markers for atherosclerotic plaque development and rupture but not restricted by that because synthetic nano-HAp has a variety of different biomedical and environmental applications [5-7]. Nanodiamonds also have a series of potential and already realized applications of fluorescence imaging and magnetic sensing of biological systems via nitrogen-vacancy defect centers [8-11].

The advantages of the multifrequency EPR and ENDOR approaches to characterize the surface located and intrinsic paramagnetic centers in nanostructures are presented in this talk.

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Thu 09-2 Study of the electron-nuclear levels anticrossings of the Ho^{3+} ion in $CaWO_4$ crystal by tunable high-frequency EPR spectroscopy

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Spectroscopic properties of the sheelite crystals ($CaWO_4$) doped with RE ions are studied for a long time. Last time there was interest in their use for quantum computing. For applications it is important that electron-nuclear sublevels in the magnetic field have the areas of anticrossings. Recently direct observation of electron-nuclear sublevels anticrossings in $LiYF_4$:Ho^{3+} which is a structural analog of sheelite was published [1]. Now we present the study of the electron-nuclear sublevels anticrossing of the Ho^{3+} ion in $CaWO_4$ crystal by tunable high-frequency EPR spectroscopy.

The measurements of anticrossings were done in the frequency region 260-290 GHz with magnetic field up to 0.2 T that corresponds to the resonance transitions from ground doublet to the nearest excited singlet of Ho^{3+} ion. It is known [1] that anticrossing can be caused either by hyperfine interaction ($\Delta m=2$) that mixes doublet and singlet states or by random crystal field ($\Delta m=0$). The report discusses these cases in detail.

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Thu 10-1

Combination of multi-frequency EPR/ENDOR measurements and DFT analysis to study the impurities in nanohydroxyapatite

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We demonstrate the application of the combined experimental-computational approach for studying various types of ionic substitutions in the structure of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ nanocrystals (nano-HAp).

Previously we have exploited the increased sensitivity and resolution of high-frequency electron paramagnetic resonance (EPR) to study the tissues of calcified aorta walls and synthesized nano-HAp samples [1-2]. Now we have spread our research onto the investigations of different nano-HAp samples by means of X- (10 GHz) and W- band (94 GHz) EPR and double resonance (ENDOR) pulsed techniques. It is demonstrated that during wet synthesis process nitrate anions from the by-products could incorporate into the nano-HAp. The comparison of the experimental data with the spectroscopic and structural information as followed from *ab initio* DFT calculations (cf. Fig.1) allowed us to determine the structure and location of NO_3^-/NO_3^{2-} defect.

We have proposed the usage of the NO_3^-/NO_3^{2-} species to probe the effects of co-doping of nano-HAp by different types of ionic substitutions. In particular, the competitive nature of interplay between simultaneously incorporated nitrate and carbonate anionic dopants was observed. Furthermore, the complexation between the oppositely charged impurities was suggested when the nitrate is introduced in the nano-HAp together with Mn^{2+} ions. All the experimental observations were supported by DFT calculations.

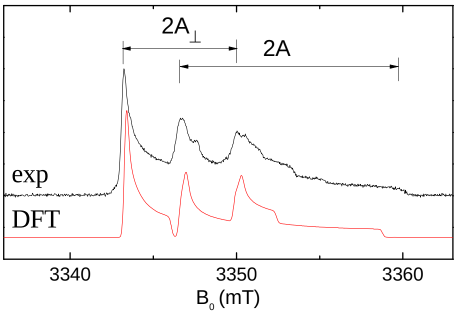

Fig. 1. Electron Spin Echo detected EPR spectrum of the NO_3^{2-} radical in nano-HAp at 94 GHz at T = 297 K (black) along with the curve simulated using the spectroscopic parameters calculated within DFT approach (red).

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[2] B. V. Yavkin et al., Pb^{3+} radiation defects in $Ca_9Pb(PO_4)_6(OH)_2$ hydroxyapatite nanoparticles studied by high-field (W-band) EPR and ENDOR *PCCP*, 2012, **14**, 2246.

Thu 10-2

Photon echo measurement of g-factors in the ground and excited states of Er^{3+} in $LuLiF_4$

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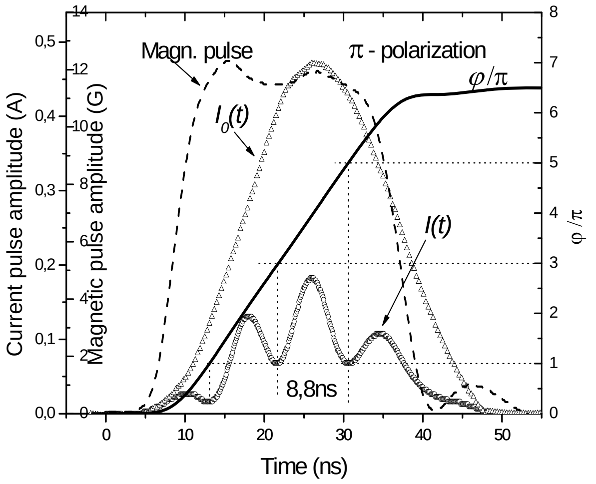
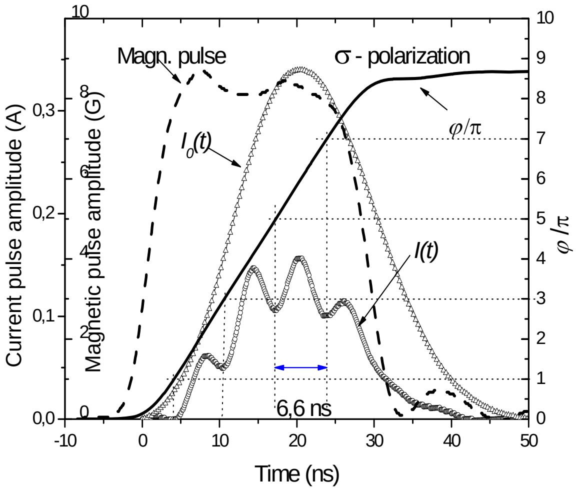
The g-factors $g_{g||}$ of the ground ${}^4I_{15/2}$ and $g_{e||}$ of excited ${}^4F_{9/2}$ states of the Er^{3+} ion in the $LuLiF_4$ in the zero dc magnetic field are determined from measurement of Zeeman splitting Z of the σ and π optical lines in a weak pulse magnetic field using precise method [1,2]. The intensity of two-pulse photon echo qualitatively can be described by the expression [1,2]

$$I(t) = I_0(t)(1+\cos\varphi(t))/2, \quad \varphi(t) = \int_{t_0}^{t} Z(t')dt, \quad Z(t) = (g_{e||} \pm g_{g||})\beta H(t)/\hbar'.$$

Here $I_0(t)$ is echo intensity without magnetic pulse, H is an amplitude of a pulse magnetic field, t_0 is the time of the beginning of pulse action, β is the Bohr magneton, $\hbar$ is the Planck constant, the plus and minus signs correspond to the σ and π laser polarizations. The pulse magnetic field is directed along the crystal axis C.





Dependences versus time of the experimental photon echo signals in the both cases H=0 and $H\neq0$ are shown for π-polarization in the left figure and for σ-polarization in the right figure. Also in these figures the pulses of a current and the calculated values of magnetic field amplitudes are shown. We select values $g_{e||} \pm g_{g||}$ so that times t_n, at which the calculated values of a phase are equal to $\varphi(t_n) = (2n+1)\pi$, approximately coincided with positions of minima of the photon echo intensities. Then we approximate experimental curves by the expression $I(t) = I_0(t)a(1+b\cos\varphi(t))/2$, find parameters a and b and then improve values $g_{e||} \pm g_{g||}$, achieving the best agreement of the calculated and experimental values of coordinates of minima. Thus we find $g_{e||} - g_{g||} = 6{,}94 \pm 0.05$ and $g_{e||} + g_{g||} = 13.12 \pm 0.05$. From here we have $g_{e||} = 10.03 \pm 0.07$ and $g_{g||} = 3.09 \pm 0.07$. The physical reasons why a≠1 and b≠1 are discussed.

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Thu 11-1

An NMR study of nanostructured ammonium 12-tungstophosphate and 12-molibdenphosphate

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Heteropoly oxometalates (POM) is a large class of stable, highly organized inorganic compounds exhibiting various properties. Although studied for over 150 years, these compounds still remain of current interest because of an exceptional variety of their structures and properties. Heteropoly oxometalates have a number of unique properties (chemical and thermal stability, high ionic conductivity, and highly developed surface) and are actively used in many scientific and engineering applications.

Since NMR spectroscopy is the most sensitive method of distinguishing between structurally different molecular groups, here we used ^{1}H, ^{2}H, ^{31}P, and ^{15}N MAS NMR spectroscopy to study the structure of ammonium 12-tungstophosphate and 12-molibdenphosphate. The ^{1}H MAS NMR spectrum of the polycrystalline salt $(NH_4)_3PW_{12}O_{40}\cdot 10H_2O$ is shown in Fig.1. The spectrum contains a signal for water molecules (δ = 4.4 ppm) and two signals for the protons of the ammonium cation. One of these signals (δ=5.2 ppm) is a triplet with the characteristic coupling constant $^{1}J_{1H—14N}$ = 57 Hz, while the other signal (δ = 6 ppm) is a broadened singlet. The presence of two types of signals for the ammonium cations in the ^{1}H NMR spectra suggests that these groups are not equivalent in the nanostructured salt. Using ^{15}N MAS NMR spectroscopy, we detected two types of ammonium cations in ammonium 12-tungstophosphate and 12-molibdenphosphate too.

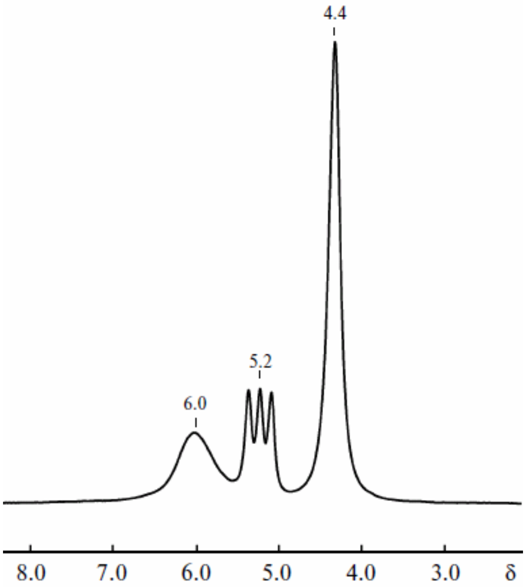

Fig. ^{1}H MAS NMR spectrum of $(NH_4)_3PW_{12}O_{40}\bullet 10H_2O$ (spin rate 20 kHz)

Comparison of the ^{1}H NMR spectra of the salts $(NH_4)_3PW_{12}O_{40}\cdot nH_2O$ and $(NH_4)_3PMo_{12}O_{40}\cdot nH_2O$ with different *n* values and the ^{1}H MAS NMR spectra of the partially deuterated salts reliably demonstrated that one type of ammonium cations is in the bulk (the triplet at δ=5.2 ppm, see Fig.1) of crystallites, while the other type is on their surface (localized on the surface of smaller spherical crystallites 7-10 nm in diameter; the low-field signal, see Fig.1). We also were the first to measure the coupling constants for the solid-state ammonium cation. To sum up, our comprehensive study of ammonium 12-tungstophosphate and 12-molibdenphosphate revealed a relationship between the morphology of nanoparticles of the crystalline salt and the hydrogen atom isotopes. The data obtained can be used to examine 12-tungstophosphate salts applied to, *e.g.*, silicon and titanium oxides, carbon, *etc*. As a result of the work were also measured the spin-spin coupling in solid state $^{1}J_{14N\text{-}1H}$ = 54-57 Hz, $^{1}J_{14N\text{-}2H}$ = 8 Hz, $^{1}J_{15N\text{-}1H}$ = 75-79 Hz, $^{1}J_{15N\text{-}2H}$ = 11-12 Hz, which factually define the geometry of NH_4^+ and ND_4^+ cations in the salts investigated.

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Thu 11-2 Time-resolved and pulse EPR study of photoexcited states of copper-containing system

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Porphyrins and their derivatives have a unique ability to bind a wide variety of metals and paramagnetic ligands and to provide a wide range of redox photophysics and photochemistry. Due to this combination of properties the porphyrin complexes are interesting in many fields of research including the conservation of solar energy and electron transfer processes [1]. Special attention is attracted to the formation of nanoscale porphyrin assemblies. The study of photo-induced spin polarization of system containing of porphyrins and their derivatives is aimed at creation of new materials which spin and magnetic properties can be controlled by the light [2].

We carried out the study of the photoexcited short-lived states of a new system constructed from zinc porphyrin molecule covalently bound to the copper ion complex by time-resolved and pulsed EPR methods. New protocol for the observation of the echo detected EPR spectrum of photoexcited short-lived states for a system with a stable paramagnetic center is proposed.

Time-resolved and echo detected EPR data and application of the nutation spectroscopy allowed us to establish that after the photoexcitation of the investigated system electron spin polarization of the triplet state of the zinc porphyrinis partially transfer to the copper states. As a result, the EPR spectra of photoinduced states are the sum of the spectra of the spin-polarized states with $S = 1$ and $S = 1/2$.

We are grateful to the Russian Foundation for Basic Research (project no. 12-03-97078-p) and Division of Physical Science, RAS (II.4) for partial financial support.

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Thu 12-1 *E''* centers in alpha-quartz

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Three oxygen-vacancy defects with electron spin *S*=1 (i.e., the *E*'' centers) have long been observed in irradiated quartz but their spin Hamiltonian parameters have quantitatively been determined only recently [1, 2]. So far we observed a dozen of *E*'' centers. After a synthetic quartz was subjected to electron irradiation (3 MeV and a fluence of 10^{17} cm^{-2}) at room temperature, the E''_{1-7} centers were observed. The intensities of the E''_{1-5} centers diminish but those of the $E''_{6,7}$ centers remain unchanged after the sample was kept at room temperature for about half a year. We noted that only the $E''_{6,7}$ centers survive after heating at 100 °C immediately after electron irradiation and both are bleached out at 150 °C [3]. The E''_8 center is revealed after heating at 100 °C and reaches a maximum after further heating at 200 °C, when the E''_9 center also appears. Further heating at 200 °C diminish the intensities of the $E''_{8,9}$ centers, which are bleached out after heating at 220 °C for 15 minutes.

Among the nine observed *E*'' centers, $E''_{1,9}$, and $E''_{3,7,8}$ have two **A**(^{29}Si) matrices each determined by using the triplet state and biradical model, respectively [1]. The E''_1 and E''_9 centers with large *D* values have the ^{29}Si hyperfine values at approximately half of those of the *E*' centers (*S*=1/2); whereas the E''_3, E''_7 and E''_8 centers with small *D* values have ^{29}Si hyperfine constants similar to the *E*' centers.

The triplet state (*S*=1) formed by two interacting spins is characterized by twice smaller hyperfine value in comparison to the single defect state (*S*=1/2) when the exchange energy is far greater than the hyperfine constant. With the increase of distance between interacting *E*' centers the exchange term decreases and becomes comparable with the strong ^{29}Si hyperfine values, resulting in hyperfine lines shift to the normal magnetic field positions (i.e. the splitting between the pair of lines at ~40 mT) of the usual *E*' centers [3]. This makes possible to determine the exchange terms by computer optimization. We note that one of the ^{29}Si hyperfine couplings of the E''_1 center matches closely in both principal values and the unique-axis direction to the E'_9 center. Similarly, these of the other ^{29}Si hyperfine couplings of the five *E*'' centers match reasonably well with those of the E'_1, E'_9 or E'_{10} centers [4].

The *E* defects are induced by particles irradiation and associated with oxygen vacancies formed in the process of atom displacements. The neutral oxygen vacancy leaves two unpaired electrons on the Si dangling bonds. The model proposed for the E''_1 center consists of two Si atoms relaxed from the oxygen vacancy, resulting in a puckered configuration [1, 2]. The set of *E*'' centers is related to the biradicals formed by two interacting *E*' centers located at various distances from each other.

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Thu 12-2 Ionic and molecular transport in polymer electrolytes studied by NMR techniques

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Electrochemical energy sources like fuel cells and lithium batteries are widely applied. The most important part of these systems is the high conductivity polymeric electrolytes. Therefore, the ionic transport nature revelation is necessary for the polyelectrolytes. Heteronuclear NMR spectroscopy and, especially, pulsed field gradient NMR technique are successfully used for ionic mobility and solvatation investigations in ion-exchange membranes and lithium conducting polymers during last ten years. These kinds of investigations are very popular, but, in spite of it, the reviewing papers are almost absent.

The transport channels forming ion-polymeric matrix, interaction mechanism, ionic and molecular self-diffusion NMR investigations are summarized. The results were obtained by the Karpov Institute of Physical Chemistry, Institute of Problems of Chemical Physics RAS, Institute of General and Inorganic Chemistry RAS and USA, Japan and Europe scientific teams.

The next polyelectrolytes are discussed: Ion exchange membranes with different polymeric matrix structures (perfluorinated membranes, styrene divinyl benzene, aromatic sulfocontaining polyamide and composite membranes); polymeric electrolytes for lithium batteries.

The translational mobilities measured by pulsed field gradient NMR are compared with the ion conductivity impedance spectroscopy data. On the basis of polymer structure, solvation particularities and ionic and molecular mobility interconnections the ionic transport mechanisms are proposed.

Thu 13-1

EPR study of the ground states structure for lithium donor centers in monoisotopic ^{28}Si

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Existence of nuclear spin of the ^{29}Si isotope leads to unresolved ligand hyperfine structure in the spectra and to additional broadening of the lines of magnetic resonance. The using of silicon enriched in ^{28}Si isotope, can make such contribution less than 4.10^{-4} Oe [1], which significantly increase the resolution in the EPR spectra, and therefore can give a more detailed study of the structure of the electronic states of defects in silicon. A striking example of isotope effects in spin resonance is the lithium center in silicon [2,3]. The inverted structure of the 1s ground state of lithium in silicon gives also a unique opportunity to study inter-valley spin-orbit interactions of donor electrons. This interaction plays an important role in spin resonance of donor states, and spin relaxation of donor electrons. It is small for lithium and increases with the increasing the atomic number of donor. In contrast to group V donors, lithium occupies tetrahedral interstitial site. Its singlet level $1s(A_1)$ is above the orbitally degenerate doublet $1s(E)$ and triplet $1s(T_2)$ states [4]. This feature allows one to investigate the structure of these states by EPR. A study of lithium doped silicon enriched in the ^{28}Si isotope (99.995%) with a low oxygen content ($N \approx 2{\cdot}10^{14}$ cm^{-3}) has demonstrated at low temperatures (T=3.8K) EPR spectra with anisotropic g factors associated with Li donor centers. The spectra were investigated without and with application of external stress to the sample and their g factors were found to be less than 2.000. The analysis of the spectra and their angular dependencies have shown that the spectrum, having g tensor components corresponding to the tetragonal symmetry, belongs to the triplet state T_2, and the other two lines in the spectrum have an angular dependence of the doublet states E. The ratio of the inter-valley spin-orbit coupling λ and λ' to the Δ parameters, characterizing the splitting of the states under internal strains have been defined by using second order perturbation approach. From the dependencies of the triplet ESR lines intensity on the external compressive stress of the crystal along the [110] it was obtained the value of the internal strains, which allowed to determine the parameters λ and λ'. Their values were found to be three orders of magnitude smaller than were obtained earlier for Li spectra with g>2 [4]. Since experimentally observed Δ value was of the order of the Zeeman splitting parameter the spectra were analyzed using the full matrix of the spin Hamiltonian for the fivefold degenerate ground state. We found that angular dependencies of the spectra observed for the triplet and doublet states with g<2 are well described by the solutions of the spin Hamiltonian with parameters λ and λ' obtained from our experimental data. At the same time, we are not able to find solutions that satisfy the data obtained for the spectra with g>2.000 in earlier studies [4].

This work was supported by RFBR: grant № 12-02-00576-a

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Thu 13-2

Nonlinear effects in magnetic resonance induced by state-dependent interactions

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Interactions of magnetic centers with each other and with the environment may depend on the quantum states of the centers. Thus, the interaction-induced shift of the resonance frequency becomes dependent on both the populations of the states involved in the respective transition and the statistics of the magnetic particles [1]. This dependence leads to nonlinear effects in magnetic resonance, e.g., the well-known Suhl ferromagnetic instability of the spectrum [2–4] and a similar surprising spectrum instability due to non-magnetic yet state-dependent interactions [5], as well as interaction-enhanced double resonance [6,7] and nonlinear spin waves. The said effects are considered on the general basis of nonlinear evolution of the spin density matrix with the population-dependent resonance frequencies. The resulting peculiar spectra have been calculated in some limiting cases. Possible applications including cold quantum gases are discussed.

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Thu 14-1 Fluoride-modified nanodiamonds studied by HF EPR

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Study of nanodiamond surface is very important task for biomedical application [1]. EPR methods are valuable to approach this task. Recent theoretical [2] and experimental [3] studies show an importance of surface modification and large influence of such modification on the both “bulk” and surface defects of nanodiamond particles.

In this research work EPR method has been applied to characterize surface paramagnetic centers. By means of high-frequency EPR and ENDOR we can distinguish up to four surface centers, by the same time proving that nanodiamond core is unchanged.

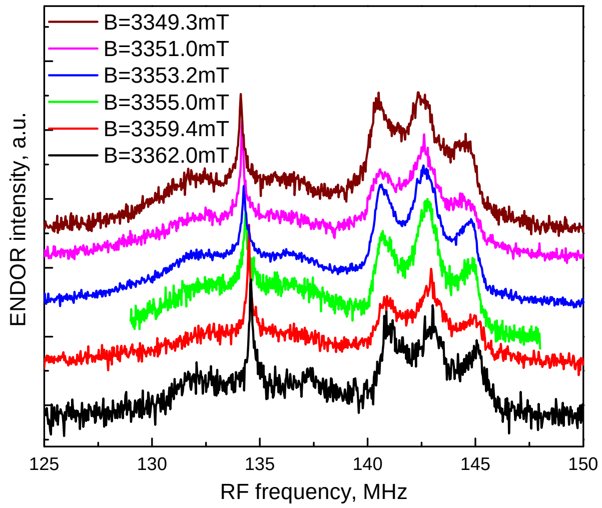

Fig. 1. Davies ENDOR spectrum of sample modified with fluorine.

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Thu 14-2 In situ EPR-spectroelectrochemical investigations of the superoxide and phenanthroline radical anion in frozen solutions

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An electrochemical one electron transfer is a nice tool for the formation of paramagnetic species, but electrochemistry does not tell us how the spin density is distributed. Therefore the combination with EPR spectroscopy is the method of choice. We will give two examples to demonstrate the power of that combination.

The superoxide radical anion usually formed by a one electron transfer to molecular oxygen plays an important role in biology and chemistry. The formation of this radical anion is usually proved by cooling down the sample to 77 K or indirectly by spin trapping. Both methods can be misleading. We have been able to detect the formed superoxide radicals [1] directly by EPR spectroscopy for the first time without changing the temperature, see Fig.1.

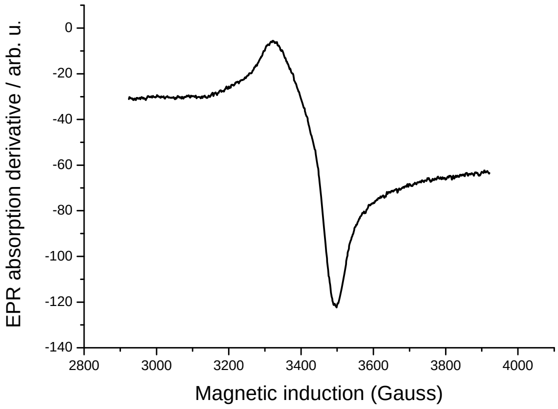

Fig.1. EPR spectrum of the superoxide anion radical at 5°C in frozen dimethyl sulfoxide. The radicals were produced by applying 3-5 µA for 2.5 h.

When a complex, built by a central metal atom and organic ligands, undergoes a one electron reduction the transferred electron can be located at the metal or at the organic ligand. We will show that in the case of the organonickel complex [NiBr(2,4,6-trimethyphenyl)(1,10-phenanthroline) most of the spin density is located at the phenanthroline ligand [2]. Remarkably the g-factors of the free and bound phenathroline radical anions differ only by 0.03 but the powder spectra show significant differences in their shape.

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Thu 15-1 Temperature-dependent exchange bias properties of PtCo/CoO bilayers

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In this talk, I will present the exchange bias properties of polycrystalline Pt_xCo_{1-x}/CoO bilayers grown by using magnetron sputtering technique. FM and AF layer thicknesses are fixed as 15 nm for both samples and composition of FM PtCo layer is changed. The chemical stoichiometry and the atomic concentrations within individual layers and the thicknesses of the samples are determined by using both x-ray photoelectron spectroscopy and transmission electron microscopy. Room and low temperature magnetization behaviors, exchange bias properties and training effects of the samples were investigated by vibrating sample magnetometry and ferromagnetic resonance. FMR experiments present uniaxial in-plane magnetic anisotropy at room temperature (Fig. 1). This behavior becomes stronger when the Pt concentration is increased. Moreover, temperature-dependent magnetization measurements demonstrate that strength and onset temperature of exchange bias are enhanced by increasing Pt concentration. Thus, the training of exchange bias is reduced. These results show that manipulation of common interface between ferromagnetic and antiferromagnetic layers gives possibility to tune exchange bias. We also discussed possible reasons for the enhanced exchange bias and blocking temperature as well as decreased training by increase of Pt concentration in FM layer [1].

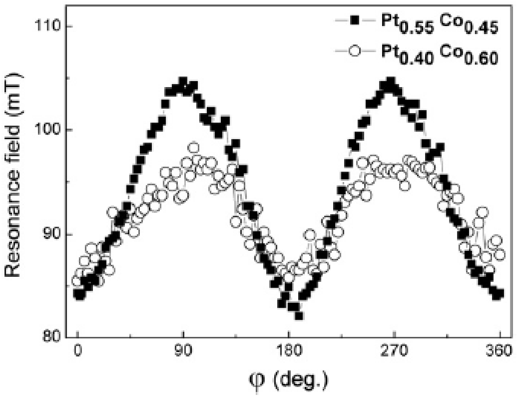

Fig. 1. The FMR resonance fields of $Pt_{0.40}Co_{0.60}$/CoO and $Pt_{0.55}Co_{0.45}$/CoO samples as a function of in-plane magnetic field angle (φ).

This work was supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) through project numbers 112T857, 106T576 and 212T217.

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Thu 15-2 EPR study of Dy-containing clusters with SMM properties

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The design, synthesis, and magnetic investigation of single molecule-magnets (SMMs) have attracted widespread attention in the past two decades because each individual molecule of SMMs can act as a single-domain nanomagnet at a certain blocking temperature in the absence of an external magnetic field, retaining its magnetization once magnetized. The SMMs show interesting physical properties and are considered promising for using in quantum informatics. The magnetic susceptibility and, in particular, AC magnetic measurements are widely used to establish SMM properties of new clusters, but there are only few examples of EPR studies of such systems. This is due to the fact that initially the attempts to create SMMs with high-temperature blocking were focused on 3d-clusters with high-spin ground states and large zero-field splitting, to study which high-frequency and high-field EPR is needed [1].

The situation is different for the Dy-containing clusters, which are promising for creating new SMMs with improved parameters.The SMM behavior of these clusters is due to the strong magnetic anisotropy which is characteristic for dysprosium ions in the low-symmetry environment at low temperature. It is well known that the ground multiplet $^6H_{15/2}$ of the Dy^{3+} ion is split by the crystal field of the nearest environment into eight Kramers doublets and the ground state at low temperature can be described by the effective spin 1/2. As a result, the EPR study of new SMMs on the basis of clusters with dysprosium ions is effective even in the X-band [2]. In spite of a great deal of interest in dysprosium compounds, the EPR studies of Dy^{3+} ions in the low-symmetry environment are almost absent.

In this work we report the results of the EPR study of a family of Fe_2Dy_2 clusters in compounds with different substituted benzoate ligands $[Fe_2Dy_2(OH)_2(teaH)_2(R\text{-}C_6H_4COO)_6]$, in which the nature and position of the substituents affect the SMMs properties [2,3] and compound is built up of Dy-Dy dimers. The EPR spectra of polycrystalline samples were measured at X- and Q-bands in the temperature range of 50 - 4 K. Experimental spectra were analyzed on the basis of the simulated spectra. The obtained data about the anisotropy of the local magnetic properties of the Dy^{3+} ion and spin-spin interactions in these cluster and data of AC susceptibility measurements allowed us to understand the origin for the change of SMM properties and the character of the effect of the spin-spin interactions on these properties.

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Thu 16-1 Magnetic properties of PrF_3 and LaF_3 nanoparticles

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Over last few years fluoride nanoparticles have been widely investigated by our group [1-4]. The sample preparation procedure was described in detail in [5]. Nanoparticles were investigated by X-ray analysis, high resolution transmission electron microscopy, nuclear magnetic, nuclear pseudo quadrupole resonance methods and electron paramagnetic resonance [1,2].

The influence of microwave irradiation on the restructuring of nanocrystalline PrF_3 powders has been experimentally analyzed by nuclear magnetic resonance (NMR) at T = 1.5 K. It is established that the relaxation times of ^{141}Pr and ^{19}F nuclei rise significantly with an increase in the hydrothermal treatment time, whereas the ^{141}Pr NMR spectra narrow, which indicates a decrease in the number of defects in the lattices of nanosamples.

The possibility of dynamic ^{3}He nuclear polarization using dielectric Van Vleck paramagnets via direct magnetic coupling between Van Vleck ion and ^{3}He nuclei was discussed earlier [6]. Reduction of particles sizes to the order of nanometers shortens the spin diffusion times over the crystal lattice. Short spin diffusion times provide the same spin temperature over whole spin system during the time of the experiment. Also, the transition from micro- to nanometers PrF_3 particles size significantly increases the surface area. Therefore, it leads to formation of the spin system with increased efficiency of the magnetic coupling between ^{3}He nuclei and the solid state substrate interface.

The main subject of the present work is studying of spin kinetics of ^{3}He in contact with nanosized crystal powders of Van Vleck paramagnet PrF_3 and its diamagnetic analogue LaF_3. The spin kinetics data of ^{3}He in contact with PrF_3 and LaF_3 nanosized powders will be reported. All experiments have been carried out by pulse NMR methods at temperature 1.5 K. The analysis of obtained data testifies in favor of cross-relaxation mechanism presence, which takes place between ^{3}He and ^{141}Pr nuclei.

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Thu 16-2

Magnetic dendrimers and spin-crossover dendrimeric iron (III) complexes

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Two types of magnetic dendrimeric systems – the liquid-crystalline poly (propylene imine) (PPI) dendrimer with γ-Fe_2O_3 nanoparticles (NPs) and spin-crossover (S =1/2 ⇔ 5/2) iron(III) dendrimeric complex have been synthesized and studied for the first time. Investigation of the first system has shown that NPs fabricated into dendrimer have an average diameter about 2.5 nm, the magnetic moment about 350 Bohr magnetons, possess the uniaxial magnetic anisotropy and "core/shell" structure [1]. A temperature-driven transition from superparamagnetic to ferrimagnetic state was observed by EPR spectroscopy with the blocking temperature about 60 K. The influence of pulsed laser irradiation on the superparamagnetic properties of γ-Fe_2O_3 NPs was also studied by EPR spectroscopy. It has been shown that irradiation of the sample held in vacuum and cooled in zero magnetic field to 6.9 K leads to the appearance of a new EPR signal, which decays immediately after the irradiation is stopped. The appearance and disappearance of this new signal can be repeated many times at 6.9 K when we turn on/turn off the laser. We suppose that the generation of conduction band electrons by irradiation into the band gap of the semiconductor γ-Fe_2O_3 NPs changes the superparamagnetic properties of NPs.

Investigation of the second system – the spin-crossover (LS, S = 1/2 ⇔ S = 5/2, HS) iron(III) dendrimeric complex allowed us to detect a novel phenomenon: magnetic - ferroelectric (MFCO) crossover, where the change of the spin state comes simultaneously with the change of the ferroelectric properties of Fe (III) centers [2]. Analysis of the magnetic behavior reflected by I versus T (where I is the EPR lines integrated intensity of the spectrum) demonstrates that iron(III) dendrimeric complex has significantly different behavior in three temperature intervals. The first (4.2-70 K) interval corresponds to the antiferromagnetic exchange interactions between LS-LS, LS-HS and HS-HS centers. The appearance of presumable magnetoelectric (ME) effect is registered in the second (70-200 K) temperature interval, whereas a spin transition process between LS and HS centers occurs in the third (200-330 K) one. The coexistence of the magnetic ordering, presumable magnetoelectric effect and spin crossover in one and the same material has been detected for the first time. The Mössbauer spectroscopy data completely confirm the EPR results.

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Fri 01 The coherent precession of magnetization

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The Bose-Einstein condensation (BEC) corresponds to the formation of a collective quantum state in which macroscopic number of particles is governed by a single wave function. The formation of this state was predicted by Einstein in 1925 [1]. The BEC of magnons was discovered experimentally in superfluid phase of ^{3}He-B [2, 3]. It manifests itself by coherent precession of magnetization. Then 6 different states of superfluid ^{3}He with BEC formation were observed. The review of various experiments on the BEC observation can be found in [4]. In all cases BEC is formed by excited non-equilibrium magnons. To excite it the pulse or continuous pumping at nuclear magnetic resonance (NMR) frequency was used.

In [5] it was assumed by Yu.M.Bunkov that the BEC formation is also possible in solid antiferromagnets $CsMnF_3$ and $MnCO_3$ with coupled nuclear-electron precession. The predictions were successfully confirmed. It was found that the coupled nuclear-electron precession shows all properties of coherent spin precession and magnon BEC [6,7]. The main experimental fact of magnon BEC evidence is the very long time of induction decay signal. It was found an order of magnitude longer than the usual induction decay. It was observed even longer than the T_2 of spin system, measured by spin echo technics. These experiments were done by means of continuous wave NMR and “switch-off” NMR. Two regimes of radiofrequency (RF) pumping were found. In the first regime the induction signal is observed after short (about 1 μs) resonant RF pulse. Let us call this pumped state as a normal. In this state spins precess with their local frequency due to the external magnetic field inhomogeneity. In the second regime the induction signal is observed after long (about hundreds of ms and longer) non-resonant RF pulse (so called “switch-off” NMR). The properties of the signal in the last case are well described in framework of magnon BEC.

Finally, the Bose-Einstein condensation of magnons and extremely long induction decay signal may be found in many spin systems with repulsive interaction of magnons. Owing to remarkable properties these systems may be considered as quantum Q-bit for quantum computers.

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Fri 02

Pressure induced magnetic order in Yb_2Pd_2Sn: occurrence of two quantum critical points

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In Yb-based intermetallic compounds, the fluctuation between magnetic Yb^{3+} ($4f^{13}$) and nonmagnetic Yb^{2+} ($4f^{14}$) can provide an additional degree of freedom on pressure- or temperature-driven ground states [1]. Such physical properties are closely related to the interaction between the 4*f* and the conduction electrons, which leads to either an ordering of the local moments through the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction or a screening of the local moments due to the Kondo effect [2]. Ternary compounds R_2T_2M (R: rare earth, T: transition metal, M: Cd, In, Sn, and Pb) are attracting much attention because of their rich variety of exotic physical phenomena, which are seemingly linked to the competition between the RKKY and the Kondo interactions [3].

Here, we report on the studies of Yb_2Pd_2Sn under the pressure up to ≈5 GPa. Two consecutive, pressure driven QCP's were detected in resisitivity and muon-spin rotation experiments. They emerge in a non-Fermi liquid environment at the origins of a domelike, single magnetic phase in Yb_2Pd_2Sn at pressures $p_{c1} \approx 1$ GPa and $p_{c2} \approx 4$ GPa. This unique behavior of Yb compounds is supposed to result from mutually competing, pressure modified energy scales, which in case of Yb_2Pd_2Sn cause a sign change of the pressure dependence of the Kondo temperature T_K and magnetic ordering temperature T_N.

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Fri 03

FMR studies of the magnetic anisotropies in half metallic and diluted magnetic oxides

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Ferromagnetic resonance (FMR) has been established as one of the most effective methods to study various properties of magnetic materials, such as the local magnetic anisotropy and exchange energies, structural properties, damping parameters, *etc*. In this respect FMR has found a wide use as effective technique to probe the nanoscale magnetic properties of spintronic (magneto-electronic) materials, which are the subject of the intense research nowadays.

In this work we give some examples of application of FMR technique to study the magnetic properties of thin films of half metallic ferromagnets (chromium dioxide and Heusler alloys) as well as the magnetic oxide (ZnO). It has been demonstrated that FMR is very effective technique to study the magnetocrystalline anisotropies, including the effects of the strain anisotropies due to the lattice mismatch between epitaxial half-metallic / oxide thin films and substrates. It has been also shown that in some cases multiple FMR modes can be observed due to the presence of the magnetic phases with different magnetic properties. Magnetic regions with different easy axis directions have been observed in the chromium dioxide. Anisotropic ferromagnetism in the oxides implanted by transition metal ions (Co, Fe) has been revealed. It has been shown that the anisotropy in the magnetic properties of the TiO_2 and ZnO thin films or plates, implanted by Co^+ or Fe^+ ions, may appear both as result of an intrinsic (substitutional ions) and extrinsic (magnetic nanoparticles) ferromagnetism. Multiple FMR modes have been observed in the systems, consisting of both intrinsic ferromagnetic phase and magnetic nanoparticles.

Fri 04 Dualism of *3d* electrons in YbT_2Zn_{20} (T=Co; Fe): ESR evidence

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The essential physics of strongly correlated electron systems is related to the competition of Coulomb repulsion and following localization of *d* or *f* electrons with hybridization of neighboring ligands which causes a *d*- or *f*-itineracy. Both the localized magnetic moments and itinerant electrons can cause the electron spin resonance (ESR) signals. Recently, the series of compounds RT_2Zn_{20} (R is rare earth ion or actinoid and T is *d*-electron transition metal) has attracted considerable attention due to a large span of intriguing physical properties.

We report a remarkable and unprecedented co-existence of the strongly anisotropic ESR spectra from the localized Co *3d* electrons and conduction electrons (*c*) in the high-quality $YbCo_2Zn_{20}$ single crystals in a broad temperature range between 4 and 300 K [1]. Our results provide the first direct evidence that ESR in a dense heavy-fermion compound with ferromagnetic (FM) correlations or static FM order originates both from localized and conducting states. It is shown that the relative contribution of itinerant electrons to the total magnetization does not exceed 9%. We show that magnetic behavior of YbT_2Zn_{20} (T=Co; Fe) and YbCuAl [2] is strongly influenced by the *3d* magnetic moments, and a weak itinerant ferromagnetism from the 3*d* sublattice only determines ESR spin dynamics at the microscopic level. Our findings on a close interplay between the valence instability of the *4f* electrons and magnetic instability of the *3d* electrons are compared with very similar results in UFe_2Zn_{20} [3], $YbFe_2Al_{10}$ [4], $YbMn_6Ge_{6-x}Sn_x$ [5], and $YbFe_4Sb_{12}$ [6] obtained by different other methods.

We argue that the ESR technique has emerged as a fascinating tool to probe the low energy paramagnetic fluctuations in dense FM *4f* and *5f* intermetallics and can be used as a rapid marker of the IV behaviour and proximity to a quantum criticality [7].

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Fri 05 ESR experiments on spin liquid phases in crystals

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Spin liquid ground state arises in magnetic crystals with specific networks of exchange paths, e.g. in low dimensional or frustrated magnets. In this strongly correlated state the ordered spin component at a crystal site is zero, however, the quantized long living excitations exist. Several types of spin liquid or related systems were discovered and studied both theoretically and experimentally during last decades. We consider a well known spin liquid system Cs_2CuCl_4, which demonstrates fractionalized S=1/2 excitations (spinons) and we report on the manifestation of the spinon continuum in ESR experiments, as well as on two types of crossovers from the spinon-type ESR to a conventional magnon-type ESR.

In the S=1/2 dielectric antiferromagnet Cs_2CuCl_4 with a distorted triangular lattice the ordering at the temperature T_N=0.62 K is strongly delayed with respect to Curie-Weiss temperature T_{CW}=4K. Besides, the spin ordering in this quasi-2D magnet is strongly reduced by zero-point fluctuations. In the temperature range $T_N<T<T_{CW}$ there is a correlated spin-liquid state with a continuum of magnetic excitations [1]. Our ESR study is performed in the frequency range 9<f<350 GHz, both above and below the ordering point. In the spin-liquid phase, it reveals a fine structure of the spinon spectrum in the Brillouin zone center in form of a resonance doublet. This doublet is a signature of the spinon continuum of S=1/2 chains with the uniform Dzyaloshinskii-Moriya interaction [2]. At cooling down to 0.05 K, for f=60-120 GHz this spinon doublet is found to survive deep in the ordered phase. On the other hand, at f<50 GHz the doublet is transformed to an antiferromagnetic resonance (AFMR) signal. The frequency of this lower crossover corresponds approximately to the main exchange integral. The coexistence of a low-frequency AFMR and of a spinon mode at a higher frequency may be ascribed to the proximity of a quantum critical point, where oscillations of an order parameter and spinons coexist. At the increase of the frequency and, hence, of the magnetic field, the spinon doublet collapses at about a half of the saturation field (i.e. above 150 GHz). Further increase of the magnetic field causes magnetic saturation and reveals a new spectrum of q=0 excitations in form of an intensive Larmor precession, coexisting with a much weaker mode of the exchange origin. This high-frequency crossover to a doublet of another kind is due to the transition from the fluctuating spin liquid to a fully polarized saturated phase.

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Fri 06 Application of ^{3}He NMR in porous media

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Nuclear magnetic resonance (NMR) of ^{3}He in porous media is a method of obtaining new information about properties of the porous substrates. The NMR characteristics of normal liquid ^{3}He strongly depend on size of volume where ^{3}He is located. The main reason for that is highly effective spin diffusion, which allows seeing space restriction starting from several mm sizes. Usually, the nuclear magnetic relaxation of liquid ^{3}He (both T_1 and T_2) takes place by means of fast spin diffusion from liquid ^{3}He to adsorbed ^{3}He and further effective surface relaxation in adsorbed layer of ^{3}He [1-5]. Thus, the ^{3}He spin kinetics and the spectral characteristics strongly depend on size of geometry filled by liquid ^{3}He. Additionally, the study of spin kinetics of ^{3}He in porous media at low temperatures is in the matter of interest due to direct magnetic coupling between ^{3}He and solid state substrate [2,6,7].

The main subject of the present work is the study of spin kinetics of ^{3}He in contact with different types of silica aerogels, charcoals, inverse opals, clay minerals and nanosized crystal powders of Van Vleck paramagnet PrF_3.

The spin kinetics of ^{3}He atoms in the silica aerogel was studied above the Fermi temperature of liquid ^{3}He. The magnetic relaxation times T_1 and T_2 for adsorbed, gaseous, and liquid ^{3}He in the 95%-porosity aerogel at a temperature of 1.5 K were obtained by means of pulse nuclear magnetic resonance techniques. It was found that T_1 in all three cases is proportional to the frequency, whereas T_2 is frequency independent. It is shown that the longitudinal relaxation proceeds due to the exchange motion in the solid adsorbed ^{3}He film. The intrinsic relaxation mechanisms in the liquid and gas phases are much weaker than the relaxation through the adsorbed surface layer [4, 8].

In the case of clay minerals, new method of determination of integral porosity of porous sample by the means of ^{3}He NMR was proposed and patented. Also, using inverse Laplace transform, the distribution of nuclear magnetic relaxation times of ^{3}He was obtained [9], which can be converted into pore size distribution, using specific models of relaxation.

As a continuation of our works of studying cross-relaxation effects in the system "^{3}He-PrF_3" nanosized crystal powders of PrF_3 were synthesized. Spin kinetics of ^{3}He in the system "PrF_3-^{3}He" was investigated. The model of longitudinal magnetization relaxation of ^{3}He nuclei was proposed in this system [10,11].

This work is partially supported by Russian Fund for Basic Research № 12-02-97048-r_povolzhie_a.

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Fri 07 Experiments on exotic magnetic phases in quasi-one-dimensional frustrated magnets

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Magnetic frustration in quantum spin chains (S =1/2) with competing nearest neighbor (NN) and next nearest neighbor (NNN) exchange interactions yields nontrivial magnetic order which attract much attention from the theoretical point of view [1-11]. The conventional magnetic order with non zero mean value of the magnetization at the magnetic ions is forbidden in 1D chains because of strong spin fluctuations even at zero temperature. In 1D chains with frustrated exchange interactions one spin correlations decrease exponentially with the distance from spin to spin. At the same time pair, triple, and multiple correlations of adjacent spins within a chain can decrease with power law behavior. In this case the phase is named the quasi long range ordered phase. An external static magnetic field H or a magnetic anisotropy in such 1D spin systems can establish true long range order with multi spin tensor order parameter [2, 5, 7, 8]. It is a compelling task to find this magnetic state with tensor order parameter in real magnetic materials. There are plausible statements about possible magnetic phases in frustrated chain magnets: the first statement is that interchain interaction in real materials can cause true long range order instead of quasi long range order in the 1D case. For instance, quasi long range ordered in the case of 1D the so called spin nematic phase starts to be long range ordered in the presence of small ferromagnetic interchain exchange interaction for the two dimensional (2D) case, as it was concluded theoretically in Refs. [9-11]. The second statement is that spin fluctuations can be strongly depressed by interchain interactions, and conventional magnetic order with non zero mean value of the magnetization at the magnetic ions occurs in the particular magnetic material under investigation. These serious restrictions give rise to the fact that, to our knowledge, tensor magnets are not observed experimentally yet.

This report will review the experimental studies of exotic magnetic phases in quasi-one-dimensional frustrated magnets. The experimental phase diagrams of these materials will be compared with the phase diagrams obtained theoretically in the frame of different models.

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Fri 08 NMR studies of superfluid ^{3}He in "nematically ordered" aerogels

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Liquid ^{3}He confined within high porosity aerogel allows investigations of an influence of impurities on unconventional superfluidity. In most of such experiments silica aerogels are used. These aerogels consist of thin strands which form a 'wisp'. NMR experiments in ^{3}He in silica aerogels have shown that both observed superfluid phases (A-like and B-like) have the same order parameters as A and B phases of bulk ^{3}He (that is, ABM and BW order parameters, respectively). It was also found that a global anisotropy of aerogel (e.g. caused by squeezing or stretching) can affect the spatial distribution of the order parameter. In our experiments we have used a new type of aerogel (the so-called "nematically ordered" aerogel) which strands are almost parallel to each other. Theory predicts that such a strong anisotropy of the aerogel can affect even the structure of the order parameter and the polar phase or ABM phase with polar distortion (both of which do not exist in bulk ^{3}He) may become more favorable than the pure ABM phase [1]. In experiments with low density (~30 mg/cm^3) "nematically ordered" aerogel it was found that the observed A-like phase has the ABM order parameter with a strong polar distortion [2]. In recent experiments, we have used another type of "nematically ordered" aerogel (Nafen), which has much larger overall density (up to ~240 mg/cm^3). The results leave no doubt that in this case the pure polar phase of superfluid ^{3}He exists in a wide range of temperatures and pressures. The obtained superfluid phase diagrams for the samples of different density will be presented.

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POSTERS

P 01 The study of the conformation and dynamics derivative of the new quaternary phosphonium salts by NMR spectroscopy

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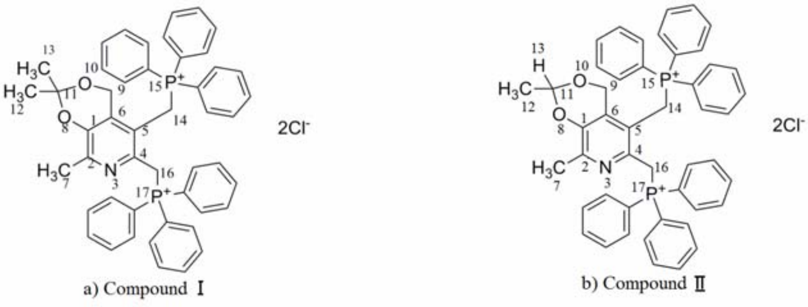
Organophosphorus compounds are widely used in medical chemistry. Among them quaternary phosphonium salts, namely vitamin B_6 (pyridoxine), are of special interest. It participates in over a hundred enzymatic reactions involved in biosynthesis, metabolism, and regulatory functions in living organisms.

Design of new biologically active substances and drugs with desired properties is impossible without the information about three-dimensional structure and dynamics of the compounds in solution. From this point of view, the method of nuclear magnetic resonance (NMR) is one of the most powerful tools for such studies. It allows one to define the spatial structure of the compounds, to investigate the dynamic processes from a qualitative point of view and, finally, to quantify the energy parameters of conformational transitions.

This work represents the study of the conformation and dynamics of some new quaternary phosphonium salts derivatives containing pyridine fragment. ^{1}H (500.13 MHz), ^{31}P (202 MHz), ^{13}C (125.758 MHz) NMR spectra of the investigated compounds 5,6-Bis[triphenylphosphonio(methyl)]-2,2,8-trimethyl-4H-[1,3]dioxino[4,5-c]pyridine dichloride (compound I, Fig.1) and 5,6-Bis[triphenylphosphonio(methyl)]-2,8-dimethyl-4H-[1,3]dioxino[4,5-c]pyridine dichloride (compound II, Fig.1) at different temperatures were recorded using Bruker "Avance -500 II TM" spectrometer.



a) Compound I b) Compound II

Fig.1. The chemical structure of the investigated compounds

Then lineshape analysis of the signals broadened by chemical exchange was carried out by WinDNMR-Pro 7.1.14 program. The activation parameters were calculated using the Eyring equation (values are presented below).

Compound I for functional groups $C\underline{H}_3$-12,13 and $C\underline{H}_2$-14,16:
$\Delta G^{\neq}$ (T_c=243K) =37.9 kJ/mol, 37.5 kJ/mol.

Compound II for functional groups $C\underline{H}_2$-14, $C\underline{H}_2$-14', $C\underline{H}_2$-16, $C\underline{H}_2$-16':
$\Delta G^{\neq}$ (T_c=243K) = 37.1 kJ/mol, 37.1 kJ/mol, 36.8 kJ/mol, 37.1 kJ/mol.

Conformational exchange between two forms obtained by simultaneous symmetrical rotation of P+-$(Ph)_3$ groups around the C5-C14 and C4-C16 bonds is observed for the studied compounds I and II. Two most stable conformations of compounds I have almost the same energies and the similar population. The contents of two the most stable conformations of compounds II in solution are different. Energetically more favorable dominant form has the concentration about 75% in solution. The content of less energetically favorable minor form is approximately 25 % in solution.

P 02 FMR investigation of iron silicide films ion beam synthesized in external magnetic field

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The modification of magnetic properties in thin films by ion irradiation is especially useful as it can be applied to locally alter magnetic properties such as saturation magnetization, magnetic anisotropy, etc. Earlier we have used magnetic-field-assisted ion-beam synthesis to produce thin ferromagnetic silicide films Fe_3Si in single-crystal silicon substrates [1]. It was shown that application of the magnetic field during the high-dose Fe ion implantation led to the pronounced in-plane magnetic anisotropy in the synthesized films. The aim of the present work is to investigate the magnetic properties of ion-beam synthesized thin iron silicide films using the method of ferromagnetic resonance.

The FMR signal is found to be dependent on the film orientation in the magnetic field similar to that found for the FMR in thin magnetic films. It was revealed that FMR line for anisotropic samples is considerably narrower than for isotropic ones (Fig.1).

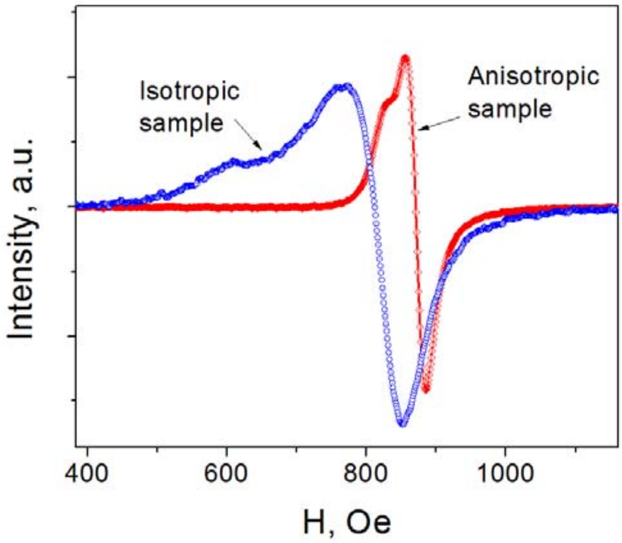

Fig.1. In-plane geometry FMR spectra of isotropic and anisotropic samples obtained at T=250 K

Moreover, for isotropic samples the FMR linewidth increases with temperature decrease. Such dependence can be explained on the basis of model of magnetic resonance in an ensemble of single-domain anisotropic particles. The approach used is based on the independent-grain model once proposed for the description of FMR in polycrystals.

It should be noted that FMR linewidth for anisotropic samples is nearly constant with temperature variation. This behavior is in a good agreement with Raikher model. When the dispersion in the directions of anisotropy axes of the particles is absent the contribution of inhomogeneous broadening to linewidth is negligible at low temperatures.

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P 03

Dzyaloshinsky – Moriya interaction and anisotropy of polaron state in EuB_6

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In this report the possible influence of super-exchange interaction on anisotropic magnetic properties of the europium hexaboride EuB_6 is discussed. EuB_6 is the well known compound with colossal magneto-resistance. We observed in $EuB_{5.98}C_{0.02}$ by ESR the magnetic phase separation and the anisotropy of the induced magnetization **M**.

The properties of f-electron compounds have great scientific interest, due to wide range of different ground states, including complex forms of magnetic order, heavy-fermion and Kondo-insulating phases. The large variety of ground states is generally attributed to the presence of strong electronic correlations. The energetic proximity of f-electron configurations may lead to valence fluctuations. The latter is yet one reason for local structure instability.

The super-exchange Dzyaloshinskii-Moriya interaction arises from spin-orbit coupling effects. The coupling between europium spins $\mathbf{S}_A$ and $\mathbf{S}_B$ on sites A and B respectively takes the form $H_{DM} = \mathbf{D}_{AB} \cdot (\mathbf{S}_A \times \mathbf{S}_B)$ where the coupling constant $\mathbf{D}_{AB} \propto (\mathbf{x} \times \mathbf{r}_{AB})$ depends on the vector $\mathbf{r}_{AB}$ connecting the site A to the site B, and on the displacement **x** of the ligand ion (boron) from the AB (Eu-Eu) line. It is clear that the Dzyaloshinskii-Moriya interaction is non-zero only for non-collinear Eu spin configuration, and when the boron atom doesn't belong to the Eu-Eu line.

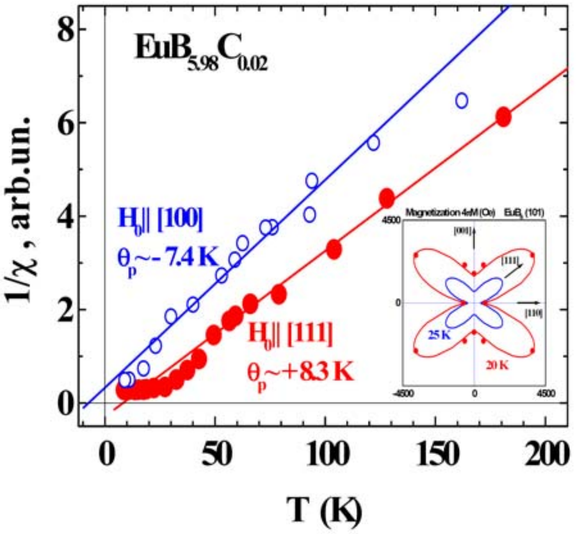

Fig.1. Temperature dependences of the inverse intensity of the ESR spectra for two orientations of the EuB_6 single crystal. Inset: Dependence of induced magnetization on crystal direction for two temperatures.

According to [1] magnetic ordering does not exclude valence fluctuations. The deviations of the susceptibility from an ideal Curie law $\chi = C/T$ are described by the Curie-Weiss law

$$\chi = C\cdot[T - \boldsymbol{\theta}_p]^{-1} = C\cdot[T - (\boldsymbol{\theta}_{mag} - \mathbf{T}_{fluct})]^{-1}.$$

Here, the Curie-Weiss temperature $\boldsymbol{\theta}_p$ is the difference between the valence fluctuation temperature $\mathbf{T}_{fluct} > 0$, and $\boldsymbol{\theta}_{mag}$, presenting magnetic correlations; $\boldsymbol{\theta}_{mag}$ is usually negative for antiferromagnetic and positive for ferromagnetic order.

If we suppose that the difference between ordering temperature and $\boldsymbol{\theta}_p$ is due to valence fluctuations, $\mathbf{T}_{fluct}$ is obtained in all cases negative. The valence fluctuations in one of the sub-lattices of the antiferromagnet or of the ferromagnet will lead to increased susceptibility and to increasing molecular field. Indirect exchange interaction between Eu ions occurs through the electrons of both bands, i.e. the conduction band and the valence band. Thus, the above indicates that in investigated compound of europium the valence instability may lead to a new type of magnetic behavior and, consequently, to the possible co-existence of magnetic phases.

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P 04 Quantum-chemical modeling of the complex between hydroxyapatite and collagen fragments

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Collagen very well represented in the body of animals and the man is an important component of the atherosclerotic formations in the body of animals and, in particular, the man. It is known that the interaction between collagen and hydroxyapatite in atherosclerotic plaque is similar to analogous processes in the bone tissue. Bone tissue is composed mainly of the collagen fibers associated with the hydroxyapatite [1]. However, the specific mechanisms of this interaction are still not established clearly.

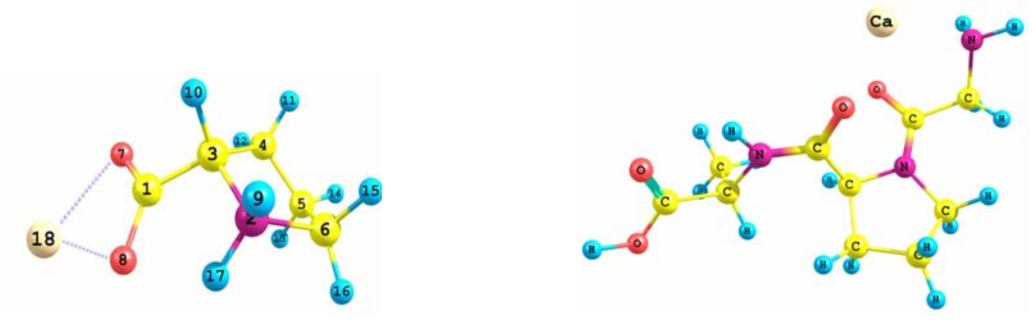
The samples of collagen fragments and hydroxyapatite were studied in this work using modern quantum chemical methods of structure modeling.

Quantum-chemical modeling of the interaction processes between the parts of aminoacid chains of collagen and the calcium ions of hydroxyapatite was proceeded. We have performed quantum-chemical calculations of electronic and spatial structures and ^{13}C and ^{1}H magnetic shielding constants for the set of model structures and their complexes with Ca^{2+}. All calculations were carried out with full optimization of all geometric parameters of the molecules in a framework of DFT method on the level of B3LYP/6-31G(d,p).

According to the literature data [2] in the process of complex formation between collagen and hydroxyapatite intermolecular bonds are formed between calcium ions of hydroxyapatite and oxygen atoms of the collagen amino acids. For studying such interactions the cis- and trans-structures of proline, lysine and their complexes with Ca^{2+} ion were investigated. We have also studied the complicated forms of molecular clusters, which are closer to the real molecular structures.

The results of DFT quantum-chemical calculations of electron and spatial structure of model compounds showed that calcium ion forms weak intermolecular bonds with the oxygen atoms of proline included in glycine-proline-alanine fragment.

Structures of the model complexes are shown in Figure 1.



(a) (b)

Fig. 1. Complex of proline (a) and Glu-Pro Ala-fragment (b) with Ca^{2+} ion

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P 05 The effects of NO-synthase inhibitor on nitric oxide production in rat brain after ischemic and hemorrhagic strokes: EPR study

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The system of nitric monoxide (NO) is one of the most studied systems of the body. NO is constantly produced in brain by constitutive isoforms of NO-synthase (NOS). In present the development of brain ischemia and subsequent stroke is associated with disorders of cerebral blood flow, as well as damages in its regulation by the NO system. In our study we conducted investigation of the role of NO in synaptic conductivity during modeling of hemorrhagic and ischemic stroke using the method of electron paramagnetic resonance (EPR). We studied the content of NO in the tissues of the rat's brain (the hippocampus) by EPR spectroscopy using the technique of spin traps. As a spin traps a complex Fe^{2+} with diethyldithiocarbamate (DETC) - $(DETC)_2$-Fe^{2+}-NO was applied.

The model of ischemic stroke was developed in male albino rats. They were undergoing to hypoxia within 5-minutes (by conditional uplifting to the height of 4500 meters above sea level). During modeling of hemorrhagic stroke animals were treated with 40 ml of autologous blood in the CA1 region of the hippocampus. The fence of the hippocampus has produced 24 and 72 hours after the presentation of hypoxic stimulus. Registration of prepared samples were conducted on the X range EPR spectrometers EMX/plus and ER 200E SRC of Bruker (9.50 GHz). There was registered the EPR signal with a value of g-factor g=2.038, which is formed by a complex $(DETC)_2$-Fe^{2+}-NO. It was found that just after modeling of ischemic and hemorrhagic stroke NO production in hippocampus has decreased by 2-3 times in 5 hours and this decrease is stored for 72 hours. The NOS inhibitor L-NAME decreases 3 times this decreased level of NO content after 72 hours ischemia and, on the contrary, it returns the level to the original level when applied in 5 hours of ischemia. The comparison of these data with the results of electrophysiological studies reveals a violation of conditions of neuronal communication and the disruption of input-output processes at the level of individual nerve cells and their populations at a reduction of oxygen voltage in the tissues of the hippocampus, which controls the memory processes and behavior. Experimental data on the restoration of the balance of input-output relations in the population of cells in the hippocampus after inhibition of NO-synthase suggests inhibition of excessive production of NO in situations, accompanied by the weakening of the delivery of oxygen to different parts of the brain.

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P 06 High-frequency EPR of Fe^{2+} ions in YAG

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Divalent ions of iron in Yttrium-aluminum garnet single crystals $Y_3Al_5O_{12}$ (YAG) have been previously studied by acoustic paramagnetic resonance (APR) [1]. It was found that Fe^{2+} replaces Al^{3+} ion in the octahedral position. For theoretical description of the spectra S = 1 effective spin was used and the Spin-Hamiltonian constants were determined.

We have undertaken broad-band (37-850 GHz) electron paramagnetic resonance (EPR) study of YAG crystal containing 1% of Fe_2O_3 at the temperature 4.2 K. External magnetic fields up to 9 kG were produced by a usual electromagnet.

In the frequency range 110 - 150 GHz we have observed the EPR spectrum typical to a singlet-singlet transition. The spectrum of Fe^{2+} is presented in Fig. 1. The field-frequency dependencies of the resonance transitions gave the possibility to measure the Zero-Field-Splitting (ZFS) between the two singlets. The angular diagram indicates that six magnetically non-equivalent positions of Fe^{2+} ions are present. It is known that such a magnetic multiplicity is observed in crystals with the rare earth ions replacing Y^{3+} ion in the dodecahedral position. Rhombic distortion of the dodecahedral position also removes the degeneracy of the non-Kramers ion, so that the electron levels of Fe^{2+} ions should be singlets. Thus we suppose that observed EPR spectrum belongs to Fe^{2+} ion located in the yttrium site.

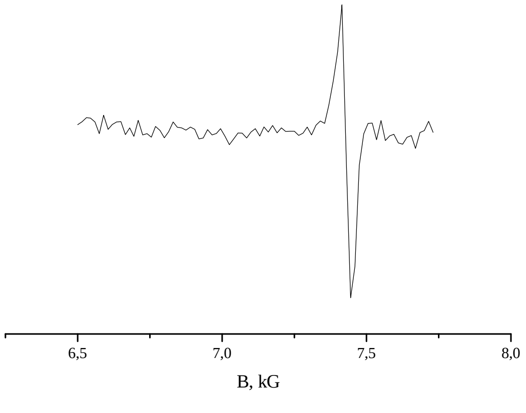

Fig.1. EPR spectrum of YAG: Fe^{2+}; frequency 140 GHz, B || [100].

Besides the singlet-singlet transition in the frequency range 240 - 300 GHz we observed also singlet-doublet transition. The EPR lines were broad and of low intensity. The ZFS of this center is in accordance with the previous work [1], however further study is necessary to confirm belonging of this center to the octahedral position of the garnet structure.

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P 07

Reorientational and translational motion of BH_4 groups in novel bimetallic borohydrides $RbCa(BH_4)_3$ and $CsCa(BH_4)_3$: results of NMR study

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Borohydrides are considered as promising materials for hydrogen storage due to their exceptional volumetric and gravimetric hydrogen densities [1], but their stability with respect to thermal decomposition and the slow sorption kinetics remain the major drawbacks for a practical use. Apart from the practical relevance, these compounds are of considerable interest as model systems for studying the correlation between atomic dynamics and crystal structure. Elucidation of hydrogen dynamics in complex hydrides may contribute to improving their hydrogen-storage properties. In this work, we report the results of the first nuclear magnetic resonance study of atomic jump motion in new bimetallic perovskite-type borohydrides $CsCa(BH_4)_3$ and $RbCa(BH_4)_3$. Measurements of the ^1H and ^{11}B NMR spectra and spin-lattice relaxation rates were performed over wide ranges of temperatures (84 – 580 K) and resonance frequencies (14 – 90 MHz).

In the studied temperature range, the proton spin-lattice relaxation rates R_1^H measured at three resonance frequencies for $CsCa(BH_4)_3$ and $RbCa(BH_4)_3$ exhibit a frequency-dependent peak near 320 K and 290 K, respectively. Such a peak is expected to occur at the temperature at which the reorientational jump rate of BH_4 groups becomes nearly equal to the resonance frequency. The reorientational motion responsible for this peak is characterized by the activation energy of 0.50 eV for $CsCa(BH_4)_3$ and 0.52 eV for $RbCa(BH_4)_3$. It is found, that for both systems some additional motional processes contribute to the low-temperature data; this leads to the presence of an additional smeared peak at low temperatures. Generally, the behavior of $R_1^H(T)$ for $CsCa(BH_4)_3$ at $T < 380$ K and for $RbCa(BH_4)_3$ at $T < 340$ K resembles that for α-$Y(BH_4)_3$ [2], where the linear coordination of a BH_4 tetrahedron by two metal atoms is believed to lead to coexistence of several inequivalent types of reorientations [3].

The reappearance of the frequency dependence of R_1^H accompanied by the increase in R_1^H with the increasing temperature has been found for $CsCa(BH_4)_3$ at $T > 500$ K and for $RbCa(BH_4)_3$ at $T > 400$ K. Such a behavior indicates the onset of an additional motional process corresponding to translational diffusion of intact BH_4 groups. This is supported by the temperature dependence of the ^1H and ^{11}B NMR line widths which drop to very small values (~ 1 kHz) at high temperatures.

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P 08 Rabi oscillations of paramagnetic ions in solids: role of electrostatic interactions

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A successful demonstration of long-living Rabi oscillations (ROs) is a necessary step before one can implement a given type of spin qubits as a part of a working quantum computer. In the case of paramagnetic ions diluted in a solid, ROs are induced by the application of mw field of resonant frequency ω_0 that creates continuous transitions between the two energy levels of the effective spin ½ [1]. Key parameter that would determine the number of coherent single-qubit operations is the decay time of ROs τ_R that depends on the strength of magnetic dipole interactions between the spins and can be evaluated as [2]

$$\tau_R^{-1} = \Delta\omega_d f\left(\omega_0\right)\ln\frac{2\sigma}{\Omega_R}, \tag{1}$$

where σ is the inhomogeneous half-width of EPR transition, $\Delta\omega_d$ is the dipolar half-width [3], $\Omega_R/2\pi$ is Rabi frequency [4], and $f\left(\omega\right)$ is the spectral density of the spin states.

The expression (1) was derived in the framework of continuum approximation and under assumption that relative positions of the impurity ions and their Larmor frequencies do not correlate. However, local defects of the crystal structure modify the *g*-factors of the paramagnetic centers, especially in the case of rare earth ions. For a pair of impurity ions separated by distance r, each one acts as the crystal defect and shifts the Larmor frequency of the other one. At r below the critical distance r_0 this shift would exceed Ω_R, and, consequently, the pair would not contribute to the observed Rabi oscillations. This effect is more pronounced in the case of heterovalent substitution that creates charged point defects. Taking position-frequency correlations into account, the calculated amplitude of Rabi oscillations increases U times, where

$$\ln U = kC/C_D. \tag{2}$$

Here C is the concentration of paramagnetic impurity ions, C_D is the total concentration of charged point defects in the crystal, k is the numeric constant that depends on the broadening mechanism. Namely, $k = 1{,}14$ for the broadening associated with random electric fields, and $k = 1{,}5$ for that of random electric field gradients. The results are then applied to obtain the corrections into the calculated decay of ROs of Er^{3+} and Nd^{3+} ions in $CaWO_4$ crystal series.

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P 09

Development of a method for separating the contributions of spin exchange and dipole-dipole interactions in the transfer of spin coherence between nitroxyl free radicals in solutions

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The high sensitivity of the EPR spectra of stable nitroxide radicals to their chemical structure, the presence of paramagnetic additives, solvent polarity makes method of EPR oxymetry an effective tool. EPR of radicals is a perspective technique for direct measurement of tissue pO_2, which has several advantages over the other existing methods for applications in which the parameter of interest is the pO_2 of tissues, and information is needed over a time course of minutes to hours, or for repetitive measurements over days or weeks.

EPR of radicals are widely known, but the description of the EPR of nitroxide radicals often use simplified algorithms that do not take into account all the processes due to exchange and dipole-dipole interactions. In paper [1] the contributions of the dipole-dipole and Heisenberg exchange interactions to the width and shape of the EPR lines are examined in detail and a new approaches to separate the contributions of these interactions is suggested. In this paper, using the algorithm proposed in paper [1], we made separation of the contributions of the exchange and dipole-dipole interactions. The study was conducted for radical solutions of tempon, depending on the viscosity of the solvent. The sample was dissolved in 60% water glycerol solution. The study was conducted using the CW EMX EPR spectrometer at temperatures of 283, 288, 293, 298 and 328K.

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P 10 Electron spin resonance in Kondo lattices

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We present a model of spin relaxation in Kondo lattices to explain the electron spin resonance (ESR) experiments in heavy-fermion compounds $YbRh_2Si_2$ and $YbIr_2Si_2$. The collective spin motion of quasi-localized f-electrons and wide-band conduction electrons is shown to be the main ingredients for understanding the ESR signal existence in these systems. The renormalization of the Kondo interaction by the high energy conduction electrons excitations leads to a common energy scale, which regulates the temperature dependence of different kinetic coefficients and results in a mutual cancelation of their singular parts in a collective spin mode. Our model successfully explains the ESR data in terms of their temperature, angular and magnetic field dependencies [1-4].

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P 11 Analysis of protein hydrolysis based on ^{1}H NMR spectroscopy

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Nowadays recycling of protein containing waste, produced by livestock and meat industry, and converting it to protein or peptide product is used worldwide. Reliable estimation of protein hydrolysis is one of the specific problems for protein hydrolysate production technology development. The degree of hydrolysis can be measured by a number of basic biochemical methods: mass ratio of the terminal amine nitrogen to the total nitrogen in the hydrolyzate; mass ratio of non-protein nitrogen in the total amount of nitrogen; spectrophotometrical method based on precipitation proteins with molecular weight more 2 kDa in 10% TCA solution or can be estimated with different types of chromatography. Since there is no universal method that can provide complete information on degree of hydrolysis, application of all of these methods could provide more accurate description of protein hydrolyses. We propose to use NMR spectroscopy for estimation of protein hydrolysis. It is known that molecules with high molecular mass (such as proteins) have rather long correlation time which leads to broadening ^{1}H NMR signals. Under the hydrolysis process proteins cleavage to fragments, which have rather small molecular weight and in ^{1}H NMR spectrum we observed a decrease in the line width (Fig.1). Thus a real time analysis of protein hydrolysis by ^{1}H NMR spectroscopy is possible [1].

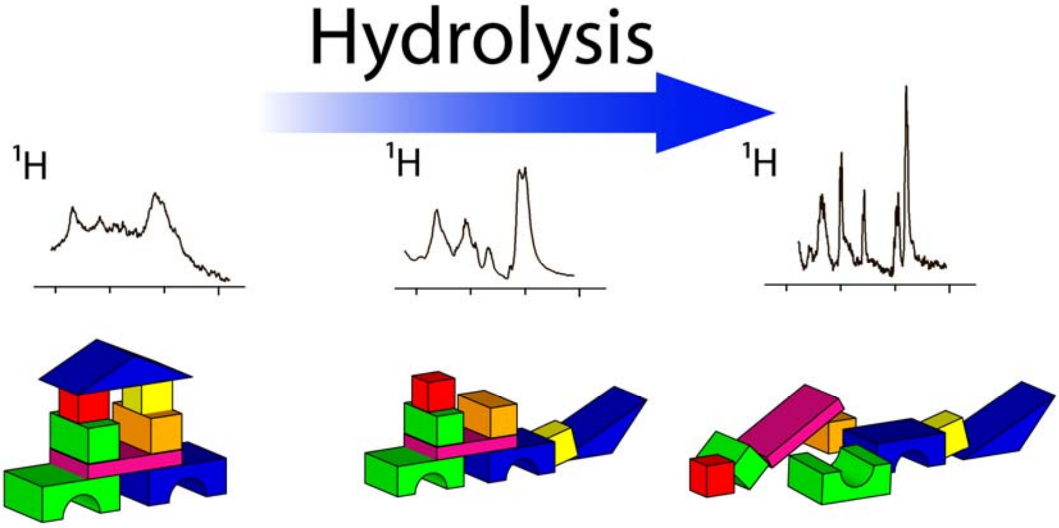

Fig.1 Scheme of changes in ^{1}H NMR protein spectra during the hydrolysis

In present paper three types of proteins (bovine serum albumin, casein and tryptone) were disintegrated under extreme conditions (~2 at., 20^{O}C = 293 K) and investigated by high-resolution ^{1}H NMR spectroscopy. Under line width analysis of the protein before and after hydrolysis we show that ^{1}H NMR spectroscopy can give details of the hydrolysis reaction and its physical/chemical parameters, information on degree of hydrolysis and fractional composition in real time. It is a good method for a subsequent investigation of hydrolysis process.

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P 12 The monitoring of sodium dodecyl sulfate micellar systems formation by 2D NOESY NMR spectroscopy

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This work describes particular NOE effect of sodium dodecyl sulfate (SDS) in monomeric and micellar systems. 2D NOESY NMR spectra of SDS in solution with concentration lower and larger than critical micellar concentration (CMC) were recorded. In the first case diagonal and cross-peaks have different signs, and the opposite takes place in the second case (Fig. 1). This work discusses theoretical background [1] of this effect and we suppose that particular of NOE can be used for inspection of SDS micelle formation during NMR researches.

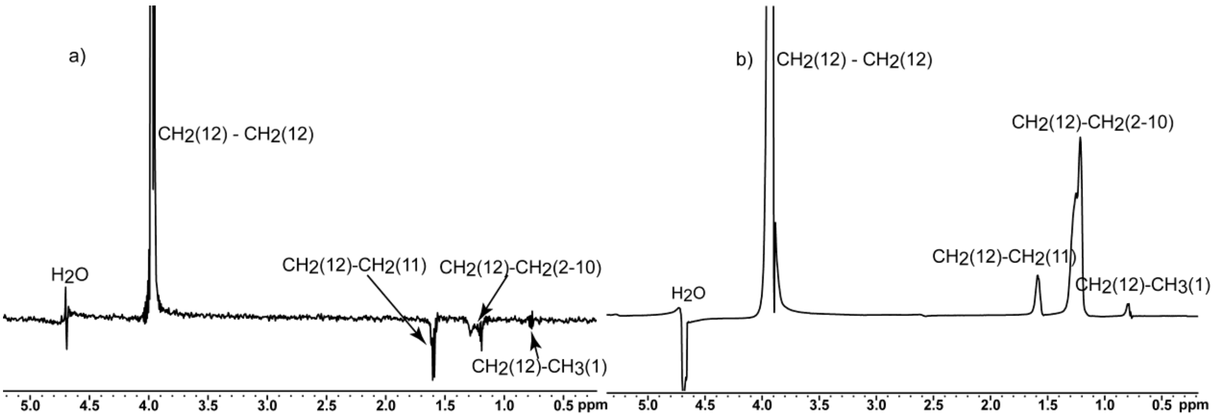

Fig. 1. Projection of sodium dodecyl sulfate 2D NOESY NMR spectra along the frequency corresponding to δ = 3.93 ppm (chemical shift of the methylene protons of CH_2 (12)) in water solution: a) the concentration of SDS in water solution is 7.6 mM; b) the concentration of SDS in water solution is 26 mM.

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P 13 Suhl-Nakamura interaction in chiral magnets

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Suhl-Nakamura interaction is the indirect interaction between the nuclear spins in magnetic materials through the spin waves in electron subsystem [1]. This interaction becomes essential at low temperature and has some specific features. Firstly, it gives quite a big contribution to the second momentum and increases the NMR line width. Secondly, it affects the temperature dependence of NMR frequency shift, which can be observed experimentally. Thirdly, the Suhl-Nakamura interaction radius is usually rather big (it may reach up to 10^3 lattice parameter). So, the existence of this interaction causes some collective nuclear effects, such as nuclear spin waves.

In this work, we present the result of our analytical approach to calculation of Suhl-Nakamura interaction in helimagnets. We started from the model of easy-plane ferromagnet with Dzaloshinskii interaction at the external magnetic field applied in the easy plane. This model is applicable for some chiral magnets, such as $Cr_{1/3}NbS_2$, and weak ferromagnets, such as $BiFeO_3$ [2]. In this model, the ground state represents the spatially modulated spin structure at small fields and periodic domain structure separated by 360° domain walls if applied field reaches some critical value. Then, using secondary quantization technique, we calculated the dispersion relations and amplitudes of spin waves. There are two types of spin waves: *d*-magnons, which are similar to the usual spin wave in ferromagnets, and *w*-magnons, which are localized at the domain walls and have two-dimensional spectrum [3]. Finally, we took into account the hyperfine interaction and got an analytic expression for the Suhl-Nakamura interactions parameter. It contains the additive contributions from spin waves of *w*- and *d*-types. It is shown that both *w*- and *d*-parts vary periodically along the helicoidal structure but these parts have essentially different dependences on external field. The contribution from *d*-magnons has weak dependence on coordinates. The external field changes the period and almost doesn't influence its amplitude. The contribution from *w*-magnons has pronounced extrema at the domain walls region. The value of extrema increase essentially when the field becomes close to critical value. The radius of the *w*-part of Suhl-Nakamura interaction also increases essentially near the critical field. The calculation of second momentum (and NMR line width respectively) due to Suhl-Nakamura interaction leads to an interesting effect. We have shown that the local NMR line width due to this indirect interaction depends on coordinates along the helicoid axis. The *d*-modes give the main contribution to the line width at the small field whereas the *w*-modes play the main role at critical fields. The integral NMR line width increases essentially in the vicinity of critical field. It is explained by the effect of *w*-magnons.

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P 14 Structure and dynamics of copper(II) complexes with bioligands by EPR and NMRD methods

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Copper is an essential transition metal ubiquitously occurring in biological systems, especially in enzymes where it is included in important active sites. Copper(II) complexes with amino acids and oligopeptides are of particular interest because they serve as models for metalloproteins and transport forms of copper in living organisms. Many reports were devoted to understand coordination characteristics of such complexes and effects of the amino acid side chains on structure, conformation, and stability of amino acids, peptides, and proteins (see e.g. Ref. [1] and references therein). But so far open questions remain about effect of side chain groups and medium properties on the hydration and dynamical behavior of copper(II) amino acid and oligopeptide complexes.

In this work structural features and dynamical behavior of copper(II) complexes with amino acids and oligopeptides were investigated by combined EPR and NMR relaxation methods. Influence of salt background on the *cis-trans* isomer equilibrium of copper(II) amino acid complexes was observed by EPR. Rotational correlation times and activation energies of rotational motion were found from temperature dependences of EPR spectra and further used to simulate NMRD profiles. From NMRD data some structural and dynamical parameters of solvation shell were derived. It was found that the exchange rate constants of axial water molecules are not lower than the value k_1 (298 K) ~$5\cdot10^9$ s^{-1} obtained for copper(II) aqua ion [2] or even higher (as was observed for $Cu(L\text{-}Asp)_2^{2-}$, $Cu(L\text{-}Glu)_2^{2-}$, $Cu(L\text{-}LysH)_2^{2+}$, and $Cu(L\text{-}Pro)_2$). The very short 2nd coordination sphere water exchange times were obtained (~4–13 ps at 298 K) for studied complexes and explained on the basis of Frank-Wen theory by quickly taking in water molecules from the 2nd coordination sphere into surrounding cavities. At the same time it was shown that carboxylic groups of aspartic and glutamic acids, alcoholic groups of serine, and ammonium groups of lysine increase the lifetimes of the 2nd coordination sphere water molecules. The same effect was observed in the case of proline probably because pyrrolidine ring of proline captures water molecules.

For confirmation of structural conclusions quantum-chemical computations of the copper(II) complexes have been performed by DFT method. On the basis of NMRD and DFT data pentacoordination of copper(II) was proposed for all complexes studied.

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P 15 Electron paramagnetic resonance in the experimental and clinical oncology

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Since 1960 different EPR approaches including spin trapping were and are used in our Institute to study the mechanisms of the chemical, radiation induced and hormonal carcinogenesis; to investigate the influence of the regulators of the cell proliferation; to diagnose and differentiate the tumors; to monitor the effectiveness of the therapeutic treatment of the malignant tumors.

Malignant tumors are induced in animals by the following chemical compounds: 2-acetylaminofluorene, 4-dimethylaminoazobenzene and N-diethylnitrosamine (liver tumors), 7,12-dimethylbenzantracene (breast tumor), 3-methylcholanthrene and benzopyrene (lung tumor). In the tight connection with the Chernobyl catastrophe an influence of external and internal (by using radionuclides) radiation exposure at low doses was studied in details. Different tissues, organs and blood of patients with breast cancer, stomach cancer and colorectal cancer were investigated to find reliable markers of the cancer progress and to estimate the influence/effectiveness of the chemotherapeutic compounds.

The EPR is sensitive to the changes in the mitochondrial electron transport chain (FeS-proteins, EPR signals with $g = 1.94$; flavo- and ubi-semiquionones with $g = 2.003$; NO-FeS complexes with $g = 2.03$), in the cell detoxification system connected with the catalytic cycle of the cytochrome P-450 – the signals with $g = 2.25$ and $g = 2.42$; NO-P-450 complexes; of the blood components with $g = 2.05$, $g = 4.25$ and $g = 6.0$; shows the presence of the NO-hemoglobin complexes with $g_{iso} = 2.01$).

Qualitative and quantitative changes of the redox state of mitochondria responsible for the reprogramming of the functioning of the electron transport chains of the animals' target cells and organs and for the development of tumors in humans could be tracked in EPR experiments. A triplet signal with $g_{iso} = 2.007$ could serve as a marker of the proliferation of the malignant tumors of various genesis and localization. A strong correlation between the mitochondrial electron transport chain defects, superoxide radicals generation rate, accumulation of the oxidative DNA damages, matrix metalloproteinases activation and vascular endothelial growth factor (which forms a malignant cell genotype and phenotype) is observed for the breast, colorectal and stomach tumors both in humans and animals.

A part of the results is summarized in the following books and papers:

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P 16 Observation of conformational exchange in cyclosporin in media of various polarities by NMR spectroscopy

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The molecule of a potent immunosuppressant drug cyclosporin A is known to change its structure and dynamical properties when dissolved in different media or bound to metal ions [1, 2]. In a polar solvents, it is stabilized by intramolecular hydrogen bonds and resembles a β-structure. Less populated conformation also exists, which is obtained from the dominant one by trans-to-cis isomerization of a peptide bond. This process is characterized by a free energy barrier of 81 ± 2 kJ/mol, and the energy of the minor conformer ΔG_0 is ~7 kJ/mol [3].

Two solvents, chloroform and dimethyl sulfoxide, offer two contrary cases of media with regard to their ability to initiate dynamical behavior of the cyclosporine molecule. They may be mixed in various proportions, and thus allow observing of the influence of solvent polarity, while the latter is changed in a consecutive manner.

It is known that an NMR spectrum of a system experiencing chemical exchange shows a certain changes while the exchange rate grows (at a given magnetic field): from separate lines of different forms (conformers) in the case of slow rate to a single line at the average frequency in the case of fast exchange rate. No such behavior was observed for cyclosporine dissolved in mixtures with DMSO : $CDCl_3$ molar fractions of 1:10, 1:4, 1:2, and 1:1. New signals appear in their characteristic chemical shift ranges and have only a small temperature dependence of chemical shifts, typical of amide protons; their intensity, in contrast, increases as the fraction of DMSO grows.

The rates of conversion of the major and minor conformers to each other, as well as thermodynamic parameters of the equilibrium, can be studied with the aid of exchange spectroscopy (EXSY [4]). Cross-peaks in 2D EXSY NMR spectra allow us to identify the chemical shifts δ of certain atoms in different conformers. Thus, the transformation described in our previous work [3] occurs in the mixed solvent: Val^5(NH) has $\delta = 7.49$ ppm in the main form and 8.36 ppm in the minor form (chemical shifts are given for the 1:4 solvent mixture and T = 38°C), $\Delta G^{\neq} = 82$ kJ/mol is the same as in chloroform, but the excess energy ΔG_0 is lower, ~2.6 kJ/mol. Within the high-frequency group of signals, the pair (8.13 – 7.96) ppm was analyzed and showed the barrier free energy of 77 and ΔG_0 of ~2 kJ/mol. Similar results were found for the exchanging pair in the low-frequency group of signals (6.89 – 6.69) ppm: $\Delta G^{\neq} = 75$, $\Delta G_0 < 1$ kJ/mol.

The observed spectra and thermodynamic parameters show that an even slower conformational exchange takes place in the presence of DMSO, since no cross-peaks uniting the major, low- and high-frequency group of signals were found. It sets an upper limit for the exchange rate of 10^{-2} s^{-1}. This process probably affects several other peptide bonds in the cyclosporin chain.

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P 17 Anisotropy of magnetic resonance characteristics of biogenic magnetite

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Magnetite (Fe_3O_4) nanocrystals of biogenic origin are very interesting objects of investigations for magnetic resonance spectroscopy. At room temperatures (T=300K) magnetite is ferrimagnetic material with inverse spinel structure.

Presently there are some experimental facts of observation of electron magnetic resonance (EMR) signals of magnetite in biological systems. The wide anisotropic signals were detected in different biological systems: cultures of dividing cells, magnetotactic bacteria, organs of navigation and magnetoreception in insects, birds and fish, in mammal and human tissues (nerve, brain, heart, liver, placenta, blood etc.) in cancer cell cultures, in tumours. Up to now the nature of such signals is not quite clear despite of heated discussions.

In our research we investigated characteristics of EMR signals for the samples of human tumors [1] and nervous tissues [2]. Our research data and literature data allowed us to determine the following characteristics of the signals.

1) One or two line components with g-value higher than 2.1 of symmetric or asymmetric Lorentz shape (in different temperature intervals) are usually observed.

2) Characteristic non-monotonic temperature dependencies of resonance field (H_{res}), linewidth (ΔH) and integral intensity (I).

3) Anisotropy of H_{res} EMR signals, which disappears near 130K.

4) The correlations between the temperature dependence of the $H_{res}(T)$ and $\Delta H(T)$ and temperature dependence of magnetite magnetocrystalline constant $|K_1|$ are detected.

To our opinion all the enumerated characteristics correspond to crystalline magnetite characteristics.

Sometimes wide EMR signals with g~5 and intensive zero field signals are observed.

Especially interesting is anisotropic behaviour of EMR magnetite signals. Angular dependencies of EMR signals were investigated in a wide interval of temperatures 100-200 K. The resonance field of EMR line is successfully described by the expression:

$$H_{res}(\theta) = \frac{\omega}{\gamma} - H_{ax}P_2(\cos\theta) - H_{cub}\left[1 - \frac{5}{4}\sin^2(2\theta) - \frac{5}{4}\sin^4\theta\sin^2(2\varphi)\right]$$

There are two contributions to the anisotropy of EMR line: axial and cubic anisotropy. Anisotropic parameters were found from the computer simulation of angular dependence of H_{res}, they changed with the temperature.

EMR anomalies within the interval 120-130K are evidently characteristic to the Verwey phase transition in magnetite.

Detected EMR characteristics in different tissues and cells are similar to the characteristics of the signals in extracted DNA [3]. Coincidence of EMR characteristics for very different biologic systems allows us to suppose, that this is some universal phenomenon in all these cases and EMR is a perfect method of detection of biogenic magnetite and may become a new method of bio-medical diagnostics of storage iron in magnetite in biological systems.

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P 18 Magnetic resonance in $Yb_{0.82}Sr_{0.18}Mn_{1-x}Fe_xO_3$ (x=0; 0,1-0,2)

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Electron spin resonance (ESR) measurements were performed in $YbMnO_3$, $Yb_{0.82}Sr_{0.18}Mn_{1-x}Fe_xO_3$ (x=0; 0,1-0,2) in a wide temperature range from 100 to 300 K. The ESR spectrum in ceramics $YbMnO_3$ consists of one exchange-narrowed line with the g-factor about g~2.11 and the linewidth about 800 Oe in the entire temperature range (Fig.1). This value of the linewidth in ceramics $YbMnO_3$ is about 2.3 times less than in $LaMnO_3$. Probably, this experimental fact is related with a change in the symmetry of the crystal structure from hexagonal $P6_3cm$ ($YbMnO_3$) to orthorhombic Pbnm ($LaMnO_3$) and thus with the change of the crystal field parameters. In the case of hexagonal structure of $YbMnO_3$ the manganese ion Mn^{3+} is surrounded by five oxygen atoms that form the bipyramid, and in the case of orthorhombic structure of $LaMnO_3$ the manganese ion Mn^{3+} is surrounded by six oxygen atoms that form the octahedron.

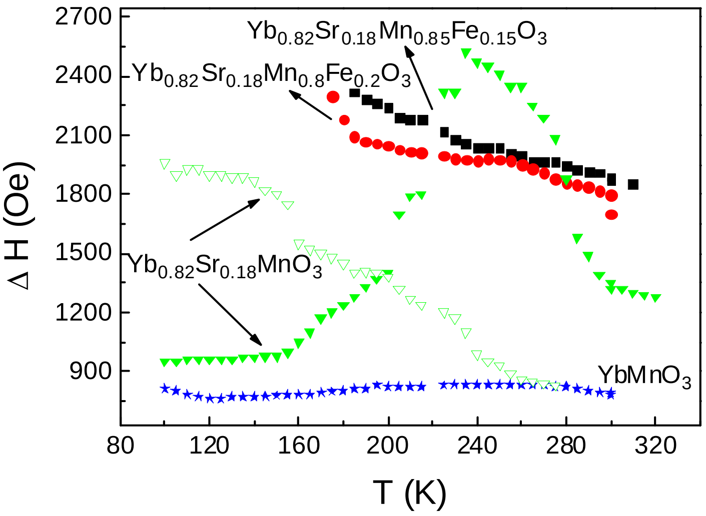

Fig. 1. Temperature dependencies of the ESR linewidth in $YbMnO_3$ and in $Yb_{0.82}Sr_{0.18}Mn_{1-x}Fe_xO_3$.

ESR spectrum of $Yb_{0.82}Sr_{0.18}MnO_3$ consists of two lines in the temperature range from 100 to 260 K due to the phase separation in the sample. At the temperature above 260 K ceramics $Yb_{0.82}Sr_{0.18}MnO_3$ goes into single-phase state (Fig.1).

ESR spectrum of $Yb_{0.82}Sr_{0.18}Mn_{1-x}Fe_xO_3$ (x=0,1-0,2) consists of one line at the temperature above ~140 K The antiferromagnetic ordering is observed in the Fe-doped samples $Yb_{0.82}Sr_{0.18}Mn_{1-x}Fe_xO_3$ (0,1-0,2) at the temperature below 140 K, thus the spectrum of magnetic resonance is not observed.

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P 19 EPR of Er^{3+} ions in Cs_2NaYF_6 single crystals

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Fluoroelpasolites having the cubic structure in the wide temperature interval are perfect model systems in which the isomorphous substitution of cations by trivalent rare-earth ions provides an opportunity to study optical and magnetic properties of dopants in a wide concentration range. Unlike widely studied chloroelpasolites (A_2BLnCl_6) doped with impurity rare-earth ions by optical spectroscopy [1-3], fluoroelpasolites (A_2BLnF_6) are studied much less. It is mainly due to the technical difficulties of their synthesis. This work presents the first results of the EPR investigation of Er^{3+} ions in Cs_2NaYF_6 and Cs_2NaScF_6 single crystals.

Crystals of cubic elpasolites Cs_2NaYF_6 doped with rare-earth ions were grown under hydrothermal conditions. For hydrothermal experiments, copper-insert lined autoclaves with a volume of ~ 40 cm^3 were utilized, and the inserts were separated by perforated diaphragms into synthesis and crystallization zones. The fluoride crystals were synthesized by a direct temperature-gradient method as a result of the reaction of the aqueous solutions containing 35–40 mol.% CsF and 8–10 mol.% NaF with oxide mixtures $(1 - x)Y_2O_3 - xLn_2O_3$ at a temperature of ~ 750 K in the synthesis zone, a temperature gradient along the reactor body of up to 3 K/cm, and a pressure of ~ 100 MPa. Under these conditions, spontaneously nucleated crystals of up to 0.5 cm^3 were grown in the upper crystallization zone of the autoclave for 200 h.

The parameters of the corresponding spin Hamiltonians, the ground states and their wave functions were determined. Structural models of the observed complexes were proposed. The experimental results were analyzed in comparison with those for the same paramagnetic ion in other hosts [4-8].

This study was supported by the grant NSh-4653.2014.2 and the Russian Foundation for Basic Research (project no.13-02-97031r_Volga region_a).

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P 20 Temperature dependence of EPR linewidth in Cs_2CuCl_4

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Recently the EPR studies in Cs_2CuCl_4 at X-band frequency showed that both angular and temperature dependencies of linewidth at temperatures $4 \lesssim T < 150\,K$ are caused by the uniform Dzyaloshinskii-Moriya interaction (DM) [1]. The high temperature estimation of linewidth at Q-band frequency confirmed an additional line broadening due to magnetically nonequivalent Cu ion positions (anisotropic Zeeman) in neighboring chains.

In present work we report on temperature dependent EPR study at high frequencies (18, 27, 34 GHz) when the influence of anisotropic Zeeman (AZ) becomes not negligible. In the approximation of weakly interacting spin chains and following the work [1], based on Anderson's theory of exchange narrowed resonance spectra, we have calculated contribution to the linewidth for AZ. The experimental data at 27 GHz and calculated linewidth for DM and AZ contributions are shown on Fig.1. As is seen the AZ gives additional line broadening as temperature decreases.

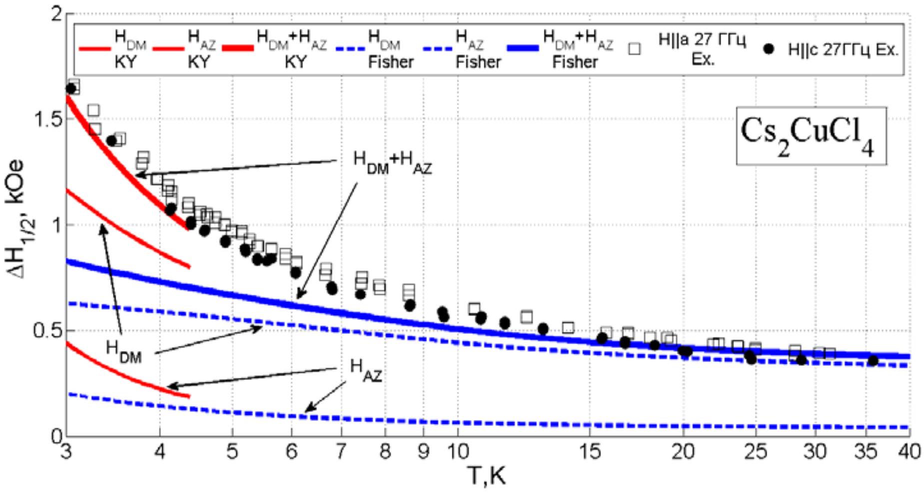

Fig.1. Temperature dependence of the linewidth in Cs_2CuCl_4 at 27 GHz ($H \perp b$): calculated using classical Fisher and quantum Kondo Yamaji (KY) spin correlations [1], experimental data (black symbols).

A good agreement with experimental polarization and temperature dependent data was found for the DM parameters D_a=6.7 GHz, D_c=7.3 GHz (g_{aa}=2.24, g_{bb}=-2.08, g_{cc}=-2.34, g_{ac}=0.32, g_{ca}=-0.08 for Cu(1), g_{ac}=-0.32, g_{ca}=-0.08 for Cu(2) positions) that coincides with ones estimated from the ESR measurements of the line position in spin liquid phase [2].

The work was performed in P.L. Kapitza Institute of Physical Problems RAS under support of the Russian Foundation of Basic Research (Grant No. 13-02-907-84).

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P 21 Structural aspects in NQR studies of covellite CuS and digenite $Cu_{1.8}S$

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Binary copper sulfides of $Cu_{1+x}S$ ($0 \leq x \leq 1$) family are numerous (≈ 15), closely related and amazing owing to variety of their physical properties. Many binary sulfides $Cu_{1+x}S$ are hardly identified by their optical properties and might be easily missed if one is to rely on the X-ray diffraction data only [1]. Therefore the structural properties of some $Cu_{1+x}S$ compounds, including digenite $Cu_{1.8}S$, are only vaguely known. The most detailed investigations on the crystal structure of $Cu_{1.8}S$ are given in a few studies only ([2] and references therein). Three polymorphic phases are reported: low-digenite below about T = 47°C, high-digenite above T ≈ 80-90°C, and a metastable transitional phase occurring between high- and low-digenite. The structures with $a \approx 5.57$ Å and space group $Fm3m$ with the sulfur atoms in sites 4a are proposed for high-digenite. There are two suggestions at the moment, how the Cu atoms could be distributed over the lattice [2]: 1 tetrahedral and 1 triangular sites only, 2 different tetrahedral and 1 octahedral sites. Low-digenite has cubic symmetry, space group $Fd3m$, with $a \approx 27\text{-}28$ Å. The S atoms form a cubic close-packed structure in the face-centered lattice. The distribution of Cu atoms was not determined definitely, but it is proposed that Cu could occupy 1 tetrahedral and 1 triangular sites (as for high-digenite) [3], 2 different tetrahedral and 4 triangular sites [4].

The preliminary NQR study of synthetic $Cu_{1.8}S$ (identified by room-temperature X-ray diffraction as digenite) shows 4 NQR spectral lines for ^{63}Cu below 200 K [5], which point to the existence of 4 non-equivalent Cu sites at least. Notably, the Cu NQR lines in the low-digenite spectrum occurs at frequencies that are close to those of the high-frequency CuS lines [6] exhibited by triangular coordinated Cu atoms. Our computation of Cu NQR frequencies for CuS based on the well established structure and point charge model (PCM) shows a good agreement with experiment [6]. PCM calculations of EFG for $Cu_{1.8}S$ based on the structural data [4] predict 4 NQR frequencies, which are similar to experimental values, for the case of different charges at all non-equivalent Cu atoms [5]. However, another model with only one triangular Cu site [3] cannot be excluded unambiguously. In practice, some Cu sites are not occupied because of non-stoichiometry of $Cu_{1.8}S$. At high temperatures Cu atoms are distributed statistically over the lattice. At low temperatures both tetrahedral and triangular units may be ordered and distorted slightly due to certain distribution of Cu, creating the superlattice observed in X-ray diffraction spectra [2]. This effect could lead also to "splitting" of one triangular site and appearance of several similar non-equivalent triangular Cu sites.

Recent experimental data and calculations are presented and discussed. This work is supported partly by Academy of Sciences of the Republic of Tatarstan (grant No. 06-149т/Г).

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P 22 EPR study nitric oxide production in rats spinal cord and heart after disorders of moving activity (hypokinesia and spinal cord injury)

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Investigations of influence of hypokinesia (restriction of moving activity) on the organism is the actual problem of physiology. The restriction of moving activity leads to morphofunctional changes in basic life-supporting systems and affects the cell genetic apparatus. During hypokinesia (HK) locomotor apparatus changes most significantly. Restriction of muscle activity is one of the most important components of symptoms of hypokinetic syndrome. The problems associated with the HK are significant at a number of diseases, first of all at spinal cord injury. Heavy spinal injury, complicated by spinal cord injury in the form of its compression, crush zone, a partial or complete tear, remains one of the most urgent medicosocial problems, because it leads to deep disability. High frequency of spine-spinal cord injury combined with the complexity of the pathogenesis of traumatic disease of spinal cord, and the current lack of adequate methods of treatment and rehabilitation of patients with consequences of severe injuries of spinal cord endure this problem beyond the purely medical aspects. There are evidences that suggest that NO actively participates in the processes of neuronal damage in trauma of spinal cord and in HK. However, at present there is no common opinion about the role of NO in the formation of HK and in the pathogenesis of traumatic disease of spinal cord. Therefore the study of the dynamics of the content of NO in the tissues of the heart, liver, brain and spinal cord at different stages of formation of the HK and pathogenesis of traumatic disease of spinal cord is very important.

The studies were conducted on white laboratory mongrel rats breeding herd. Using the method of EPR spectroscopy, studied the content of NO in the tissues of the heart, liver, brain and spinal cord were carried out. The complex of Fe^{2+} with diethyldithiocarbamate (DETC) - $(DETC)_2$-Fe^{2+}-NO was used as a spin trap. Registration of signals from prepared samples was conducted on the X-band BRUKER EPR spectrometers EMX/plus and ER 200E SRC. We have found that the amount of NO produced in the tissues of the ventricles and atria of the heart and the liver after 30, 60, and 90 days of HK increases in 2-3 times. It was also shown that in 3 days after injury of spinal cord the level of NO production in tissues of spinal cord was 3 times higher than that for intact animals. Later on some decrease of the production level is observed, but it still remains about 2 times higher than the reference values.

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P 23 Manifestation of energy level anticrossing in EPR of spin clusters

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The EPR spectra of dimer fragments formed by paramagnetic particles with anisotropic g-factor were simulated. It is shown, that in addition to conventional EPR lines in the vicinity of energy level anticrossing one additional line can appear. Width of the line is proportional to the value of anticrossing. This line is noticeable for the system with strong anisotropy of g-factor. The appearance of the line is associated with increasing of absorption probability in the vicinity of level anticrossing.

We are grateful to the Russian Foundation for Basic Research for financial support (project no. 13-02-01157) and the President of the Russian Federation (grant no. NSh-4653.2014.2).

P 24

Structure and chemical shifts of ortho-and para-diazines in aqueous solution on the basis of density functional theory and *ab initio* molecular dynamics

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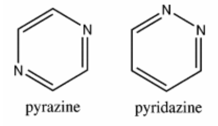
Study of the influence of dynamic processes on the properties of molecules in condensed phase is an actual problem. Quantum-chemical calculations of the optimized structure of molecular clusters can not describe the real situation in the cases which would take into account solution molecules' fluctuation in time. In this work *ab initio* molecular dynamics methods were used to study the structures of molecular clusters of diazine derivatives in aqueous solvate as function of time, temperature, the number of molecules in solution and as a result, an obvious impact of these parameters on the chemical shifts of the solute molecule.



Optimized structure of diazine in ortho- and para-position was calculated for gas phase, for the first and second aqueous solvate shell and for cluster diazine surrounded by 25-28 water molecules within the supermolecular model. Optimization of space structures was carried out by semiempirical method AM1 and density functional theory method (DFT) with functional PBE and 3z basis set by using Priroda program [1]. The spatial and electronic structure of cluster of diazine molecule with water molecules has been calculated also in periodic condensed matter with boundary conditions with using DFT method in the plane waves basis set in VASP program (part of the software package MedeA [3]). We conducted a comparative geometric analysis for isolated molecule and molecule in condensed matter, as well as analysis of changes in magnetic shielding constants for isolated molecule and for molecule in condensed matter.

For these systems an *ab initio* molecular dynamics method have been also applied for the purpose of studying dynamical processes in solution in dependce on time and temperature and the influence of these processes on the chemical shifts. Dynamic simulations were performed using the software package Vienna Ab-initio Simulation Package (VASP 5.2.2 [2, 3]) by DFT method using PBE functional in the plane-wave basis, cutoff was chosen 500 eV. For configurations obtained in molecular dynamics method the calculations of nuclear magnetic shielding constants were performed by using gauge-invariant atomic orbitals method and PBE and B3LYP functionals [1]. The results of calculation are compared with experimental data [4].

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P 25

ESR in $LiCu_2O_2$

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The quasi-one-dimensional helimagnet $LiCu_2O_2$ was studied by electron spin resonance method in a wide temperature range from 4K to 300K. All experimental data can be described in terms of the model of one-dimensional chains of copper Cu^{2+} ions, which pairwise interact with each other, as predicted earlier [1]. Fig.1 shows the fitting of the angular dependences of g-factors and ESR linewidth in $LiCu_2O_2$ in three crystallographic planes at room temperature in X-band using this model. Energy levels, g-tensor and crystal field parameters, including the contribution of point charges, exchange contribution and contribution related with the dipole moments of neighboring oxygen atoms, were calculated for $LiCu_2O_2$. The obtained theoretical values of g-factors are consistent with experimental data.

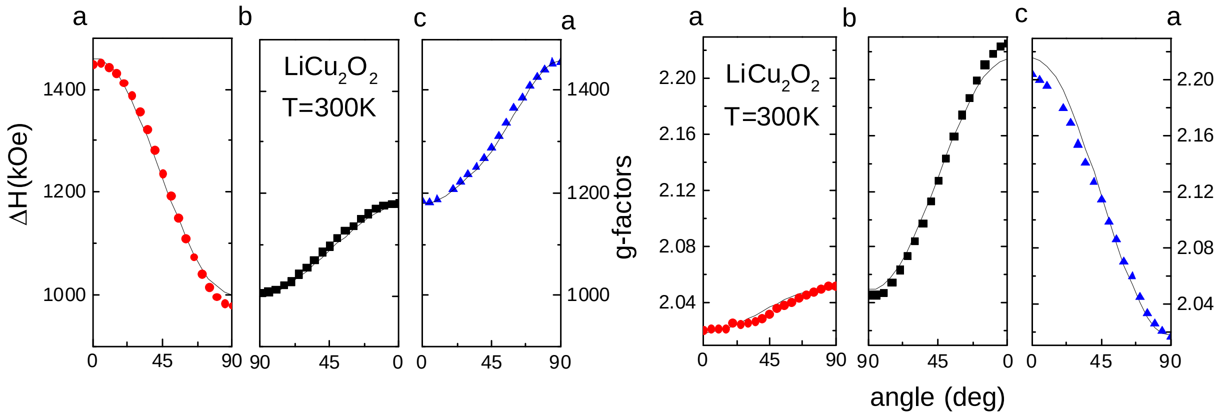

Fig. 1. Angular dependencies of g-factors and ESR linewidth in $LiCu_2O_2$ in three crystallographic planes at room temperature in X-band.

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P 26 Observation of Majorana quasiparticles edge states in superfluid ^{3}He

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Majorana fermions are particles identical to their own antiparticles [1]. Up to date stable particles with Majorana properties have not been found. Recent investigations suggest that quasiparticles in special class of condensed matter could be Majorana fermions [2]. Among other systems, Majorana quasiparticles are predicted to exist at the edges of superfluid ^{3}He [3, 4] with a power-law dependence of the physical quantities on temperature. Several experimental approaches were suggested to detect Majorana quasiparticles edge states in superfluid ^{3}He [5-7]. So far only Grenoble experiments have shown the direct observation of Majorana quasiparticles influence on superfluid ^{3}He-B properties at the limit of ultra low temperatures [8]. In these experiments the temperature dependence of the bulk Bogolyubov quasiparticles heat capacity and the edge Majorana quasiparticles heat capacity were separated. It was found that at ultra low temperatures down to 0.13 mK the Majorana quasiparticles constitute a part of 15% of bulk ^{3}He-B heat capacity. The recent progress in these investigations will be reported. New experimental conditions and approaches will be discussed. The point is the Majorana quasiparticles at the edges of superfluid ^{3}He-B may have interesting magnetic properties [5]. That is why the attempt to detect these states by means of nuclear magnetic resonance (NMR) of ^{3}He-B is perspective task, especially with the help of Q-ball [9, 10] at the world record limit of ultra low temperatures. Recently, the additional surface relaxation mechanism of Q-ball was observed [10]. In light of our detection of Majorana quasiparticles at the edges of ^{3}He-B it would be interesting to study this surface relaxation mechanism in more detail.

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P 27 EPR and optical spectroscopy of cubic Ce^{3+} in Cs_2NaYF_6 single crystals

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The electron paramagnetic resonance (EPR) spectrum of Ce^{3+}ions ($4f^1$ configuration) in cubic single crystals has been the subject of a few investigations [1-3]. The same refers to experiments on optical spectroscopy of cubic Ce^{3+} ions [4, 5]. Fluoroelpasolites (A_2BLnF_6) having the cubic structure in the wide temperature interval are perfect model systems in which the isomorphous substitution of cations by trivalent rare-earth ions provides an opportunity to study optical and magnetic properties of dopants in a wide concentration range. A_2BLnF_6 are studied much less. It is mainly due to the technical difficulties of their synthesis. This work presents results of the EPR and optical investigation of cubic Ce^{3+} ions in Cs_2NaYF_6 single crystals.

Crystals of cubic elpasolites Cs_2NaYF_6 doped with rare-earth ions were grown under hydrothermal conditions. For hydrothermal experiments, copper-insert lined autoclaves with a volume of ~ 40 cm^3 were utilized, and the inserts were separated by perforated diaphragms into synthesis and crystallization zones. The fluoride crystals were synthesized by a direct temperature-gradient method as a result of the reaction of the aqueous solutions containing 35–40 mol.% CsF and 8–10 mol.% NaF with oxide mixtures $(1 - x)Y_2O_3 - xLn_2O_3$ at a temperature of ~ 750 K in the synthesis zone, a temperature gradient along the reactor body of up to 3 K/cm, and a pressure of ~ 100 MPa. Under these conditions, spontaneously nucleated crystals of up to 0.5 cm^3 were grown in the upper crystallization zone of the autoclave for 200 h. The purities of the utilized oxides were 99.99% for rare-earth oxides.

The parameters of the corresponding spin Hamiltonians, the ground states and their wave functions were determined. Structural models of the observed complexes were proposed. The experimental results were analyzed in comparison with those for the same paramagnetic ions in other hosts.

This study was supported by the grant NSh-4653.2014.2 and the Russian Foundation for Basic Research (project no.13-02-97031r_Volga region_a).

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P 28

Study of the organic molecules distribution in porous space glasses Vycor

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Study of the processes of interaction of adsorbed molecules with the surface of porous materials is an important task. Most articles on the study of porous materials such as zeolites, porous glass, aerogel, are based on the study of the properties of the adsorbed fluid in the completely filled pore space. Upon partial filling of pores, particularly at the concentrations appropriate for completing the monolayer surface of the porous material, it becomes possible to study in more detail the processes of interaction of the adsorbed fluid and the surface of the porous material.

Melting-crystallization processes and the relaxation times of cyclohexane and dimethyl sulfoxide adsorbed in porous glasses Vycor are investigated by NMR in a wide temperature range. The analysis of the temperature dependence of the relative amount of the amorphous component p_a (T) (Fig.1) has revealed that the molecules of the adsorbed fluid below the melting temperature at concentrations corresponding to monolayer filling may be part of different "phases": 1) the molecules in the crystalline state, 2) the molecules in amorphous "nonfrozen" layer, 3) molecules in the amorphous state at the surface which are not included in the "nonfrozen" layer, and 4) the molecules in the micropores.

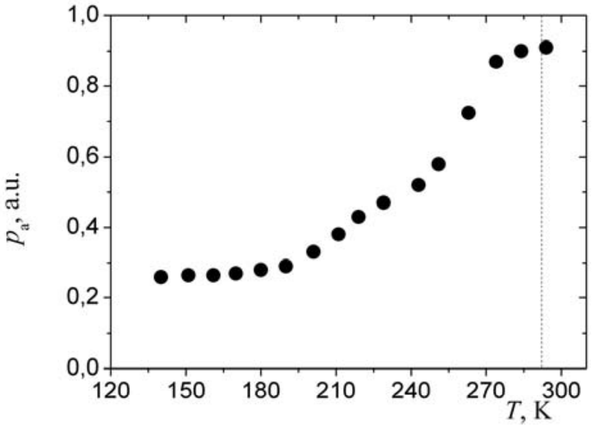

Fig.1.The temperature dependence of the relative amount of the amorphous component p_a of dimethyl sulfoxide adsorbed in porous glasses Vycor with an average pore diameter of 11 nm. The vertical line corresponds to the melting temperature of bulk DMSO.

It has been established that the adsorbed molecules form aggregates or clusters of different sizes depending on the polarity of the adsorbed fluid. In addition, for non-polar molecules, this effect leads to a nonuniform distribution of the adsorbed molecules in the volume of the porous medium. At the same time the polar liquid forms clusters of 3 nm size which are uniformly distributed in the volume of the porous glass.

P 29 Dynamics of nitric oxide production under condition of spinal cord injury in acute and chronic periods

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Rehabilitation after spinal cord (SC) injury is one of the actual questions of modern medicine. High frequency of spine-spinal cord injury is combined with the complexity of the pathogenesis of traumatic disease of spinal cord and insufficient effectiveness of treatment methods. Practically full disability of the patients and the enormous costs of treatment and rehabilitation bring this problem beyond the purely medical aspects. Morphological study of the injured SC indicates that tissue damage is not limited by the area of influence of destructive forces, and, occupying the primary intact areas, leads to the formation of more extensive damage. This process involves the brain and the peripheral and vegetative nervous systems. Various rehabilitation measures in some cases significantly improve outcomes of injury and improve the quality of life of the victims, but cannot eliminate heavy neurological deficit.

The great interest is attracted to the participation of free radical compounds of nitric oxide (NO) in the mechanisms of the development of various pathological conditions. At present there is no clear opinion about the role of NO in pathogenesis of traumatic disease of the spinal cord: it is able to mediate both regulatory and cytotoxic effects. It is believed that hyperproduction of NO by inducible form of NO-synthase initiates delayed damage of the spinal cord cells leading to their apoptosis. At the same time there is an opposing point of view according to which the excess of NO is a compensatory factor. Previously we have shown that in conditions of hypokinesia the production of NO in heart, liver and spinal cord of rats increases. Therefore, using EPR spectroscopy, we have carried out a study of the dynamics of changes in the levels of NO in the tissues of spinal cord of rats in acute and chronic periods of traumatic disease of spinal cord.

It was shown that in the acute period (in 3 days after injury) the level of NO production in tissues of spinal cord was, in average, 3 times higher than that for intact animals. Later on some decrease of the production level is observed, but it still remains about 2 times higher than the reference values. Thus, the acute spinal cord injuries are accompanied by a significant increase of NO production, which is maintained in chronic period of a disease.

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P 30 Ferromagnetic nanoparticles under asymmetric quantum stochastic resonance conditions

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Stochastic resonance phenomenon has been well investigated in various areas, including magnetic nanoparticles systems. In some previous papers the effect was considered as application to superparamagnetic particles, with noise intensity measure being temperature of the sample and external periodic signal being weak radiofrequency field [1,2]. The influence of additional permanent magnetic field, applied at different angles to the “easy axis”, to dynamic magnetic susceptibility was also thoroughly explored before [3,4] for thermal switching mode in the framework of the two-state model.

Here we present our calculations for output signal-to-noise ratio (SNR) of the system of fine ferromagnetic (iron) nanoparticles with auxiliary permanent magnetic field applied at arbitrary angle. Along with dynamic magnetic susceptibility, SNR is the most important characteristic of stochastic resonance. As well as in [5,6] we consider subbarier switches of the particle magnetic moment (due to the macroscopic quantum tunneling phenomenon) as internal noise of the system, and output signal is assumed to be regular part of the magnetic moment motion at frequency of external weak radiosignal. We obtained analytical expressions for the SNR as a dependence on some parameters of the system, including strength and direction of the auxiliary permanent magnetic field.

We also have obtained analytical expressions describing dependence of thermal noise intensity on some external and internal parameters of the system of ferromagnetic nanoparticles, including value and direction of additional permanent magnetic field, under conditions of stochastic resonance. The ratio of output power of the modulated system to output power of the non-modulated system reveals non-monotonous dependence on temperature with a distinct minimum.

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P 31

The intermolecular interactions of Fe(III) complexes with tetradentate N_2O_2 donating Schiff-base ligand

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The Fe(III) compounds with tetradentate Schiff-base ligand [Fe(III)(Schiff-base)(L)]Y have very different structural and magnetic properties. The mononuclear complexes of Fe(III) in various spin states and dimers, linear chains, hydrogen-bonded chains, a ‘hybrid’ 1-D chain-and-dimer compounds and other structures were observed in this series under variation of equatorial Schiff base ligands, axial ligands L and outersphere anions Y [1-3]. Noticeable interest is creation of magnetic materials in which the switching of spin states of Fe(III) ions leads to a change in the character of magnetic ordering. The study of influence of the composition and synthesis conditions on the complexes Fe(III) magnetic properties and on the nature of magnetic interactions between them is a necessary step in solving this problem.

In the present study the compounds $[Fe(Salen)(Pyr)_n]BPh_4$ (**1**), $[Fe(Salen)(Pyr)(Salen)Fe](BPh_4)_2$ (**2**) and $[Fe(Acen)(Pic)_2]BPh_4{\cdot}nH_2O$ (**3**) were synthesized and studied by EPR and magnetic susceptibility methods in the temperature range (5-300)K.

It is found that the change of the ratio (Salen):(Pyr) under the synthesis of samples **1** (1:1) and **2** (1:2) leads to the formation of different crystal structures. It is confirmed by X-ray measurements. The data obtained by EPR and magnetic susceptibility for sample **1**, interpreted on the assumption that the ions Fe(III), associated molecules (Pyr), form a linear chain with an antiferromagnetic interaction $J \sim -40$ cm^{-1}. In sample **2** the ions Fe(III) form binuclear complexes bridged by molecule Pyr. EPR signal from the $S = 3$ multiplet with fine structure parameters $D = 650$ Oe and $E = 5$ Oe is observed. Detection of the magnetization hysteresis in a low temperature range and the difference of magnetization measured in FS and ZFS modes indicate that the studied compound has a weak ferromagnetism in low-temperature range. This feature is consistent with increasing integrated intensity of the EPR spectrum below 10K.

Sample **3** was prepared by the technique similar to that described in [4], but using hydrated solvent. The existence of strong ferromagnetic interactions between complexes of Fe(III) in the sample **3** is found, in contrast to their properties in the non-hydrated [Fe(acen) $pic_2]BPh_4$. Ferromagnetic ordering in the sample at $T < 100$ K are confirmed by measurements of the temperature and field dependence of the magnetization of the sample . Temperature dependence of the magnetic resonance signal integrated intensity is explained by the transition of a part of the high-spin ions in low-spin state with decreasing temperature below 100 K.

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P 32 1D and 2D NMR investigation of alkylphosphonates

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Catalytic hydrophosphorylation of alkynes brings series of products. The structure elucidation of these molecules can be done by both NMR and MS. This task, especially for isomeric alkylphosphonates, required additional methods of investigation even after chromatographic separation. A combination of 1D and 2D NMR methods was used.

As basic methods we used standard ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and 2D COSY, TOCSY, NOESY, ^{1}H-^{13}C HSQC, HMBC and ^{1}H-^{31}P HMBC spectra. For detailed analysis we took ^{1}H homodecoupling with ^{31}P inverse gate decoupling, COSY$\{^{31}P\}$ and TOCSY$\{^{31}P\}$ for spectra simplification.

Further research was focused on identification of minor compounds and byproducts.

1D and 2D NMR spectra for a broad range open possibilities for quantification and detailed analysis of mixtures. This approach was useful for conducting mechanistic studies.

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P 33 Optical and EPR studies of the rutiles (TiO_2) colored in green or orange tones by implantation with Co ions

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Single-charged Co^+ ions with energy of 40 keV were implanted into monocrystalline (100)- and (001)-oriented plates of rutile (TiO_2) to the fluence of 1.5×10^{17} ion/cm^2. As-implanted rutile plates showed the dark grey color due to radiation-induced damages of crystalline structure of TiO_2. Then Co-implanted plates have been annealed in air at T=950°C during 1 hour for the recovering of TiO_2 crystal and optical activation of Co implant in rutile lattice. It has been found that high-temperature annealing of Co-implanted samples results in the color change to light-green tones in the annealed (100)-TiO_2 plate or to red-orange tone in the annealed (001)-TiO_2 plate, respectively. Optical spectroscopy and ESR techniques have been applied to study a nature of coloration, valence state and structural positions of the implanted Co ions in the rutile. It was established that optical absorption bands connected with the $O^{2-}\rightarrow Co^{2+}$ and $Co^{2+-}\rightarrow Ti^{3+}$ charge transfers determine light-green or red-orange colors of Co-implanted rutile samples. Also two equivalent centers related to paramagnetic Co^{2+} ions with hyperfine structure have been observed in the ESR spectra at temperature below 30 K (Fig.1). The analysis of angular dependences of ESR signals with aid of computer modeling showed that Co^{2+} ions substitute Ti^{4+} cation in tetragonal structure of the rutile. Remarkably, we have obtained a set of spin Hamiltonian parameters which is slightly different from the spin Hamiltonian parameters for Co^{2+} centers in bulk TiO_2 crystal. This difference have been attributed to the crystal structure imperfections of Co-implanted rutile samples due to formation of oxygen vacancies located near the Co^{2+}dopant ions.

The work was supported by RFBR, grants No13-02-97046-r_volga region.

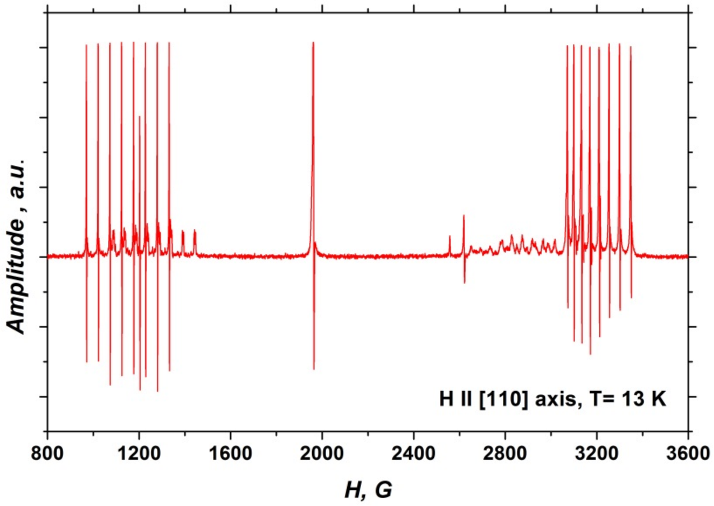

Fig.1 EPR spectrum of (001)-TiO_2 sample colored in red-orange tone by Co ion implantation with subsequent annealing in air at T_{ann}= 950 °C for 1 hour.

P 34 Influence of impurity and phonon scattering on the conduction electron g-factor in silicon

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It is known that observable semiconductor parameters such as carriers' effective masses and band gaps depend strongly on temperature and donor concentration as a result of interaction with phonons and impurity centers [1]. However such a manifestation of different many-body interactions is not well studied for the electron *g*-factor. So, in this work temperature and doping impurity concentration dependence of the conduction electron *g*-factor in silicon is investigated both experimentally and theoretically.

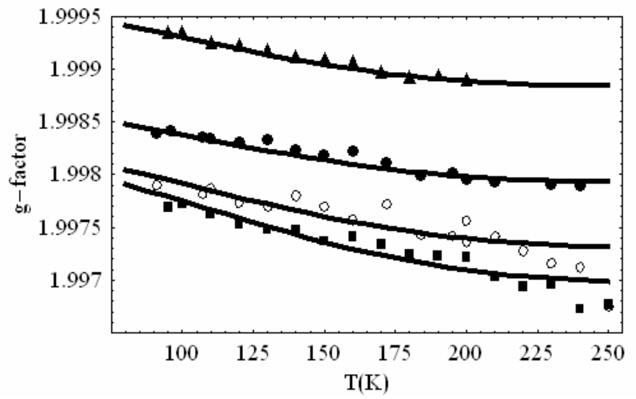

Fig.1. Measured (symbols) and corresponding calculated (solid lines) temperature dependences of the conduction electron *g*-factor in n-type Si samples doped with phosphorus (●, ○, ■) and lithium (▲). Phosphorus and lithium concentrations are $3.3\cdot10^{18}$ (●), $9.1\cdot10^{18}$ (○), $1.1\cdot10^{18}$ (■), and $3.7\cdot10^{18}$ cm^{-3}, respectively.

Experimental investigations of the electron *g*-factor are performed in conduction electron spin resonance (CESR) spectra measurements on the spectrometer "Bruker EMX 10/12" using helium cryostat with a system of a temperature control (3.8-300 K) "ER 4112 HV". We observed the conduction electron *g*-factor in silicon as a function of temperature and found that in temperature range 80 – 250 K it is similar for different donors and their concentrations. We compared CESR spectra in Si samples with different concentrations of phosphorus from ~10^{16} to ~10^{19} cm^{-3}, where the *g*-factor decreases as an almost linear function of the donor concentration.

Experimental results presented here (see Fig.1) suggest that all perturbing agents in the system can affect the *g*-factor, what could be studied in a common manner. Our theoretical consideration is based on the renormalization of the electron energy due to interaction with lattice vibrations and impurity centers [2]. Within the framework of a many-body picture the renormalization of excitation energies by the thermal or static disorder is represented by

$$\varepsilon(\mathbf{k}) = \varepsilon^{(0)}(\mathbf{k}) + \mathrm{Re}\Sigma^{*}(\mathbf{k},\varepsilon), \quad (1)$$

where $\varepsilon^{(0)}(\mathbf{k})$ and $\varepsilon(\mathbf{k})$ are unperturbed and renormalized electron energies, respectively, $\mathrm{Re}\Sigma^{*}(\mathbf{k},\varepsilon)$ is the real part of the proper self-energy, which describes influence of the perturbation on the energy spectrum. Taking into account also the Zeeman term, which contains the single electron *g*-factor $g(\mathbf{k})$, that should be considered as a function of the wave vector, one can find how disorder influences the position of the CESR line. The results of our calculations are in good agreement with experimental data (see Fig.1).

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P 35 EPR of cubic Ce^{3+} in $CsCaF_3$ single crystals

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Dielectric crystals activated with Ce^{3+} ions are promising as active media of tunable ultraviolet lasers. However, to date the number of such media is low. In particular, the number of studies of Ce^{3+} ions with cubic symmetry (CaO, SrO, BaO, Cs_2NaYCl_6, Cs_2NaYCl_6) is extremely limited [1-3]. The observation of the EPR spectrum of Ce^{3+} in a site of local cubic symmetry is of special interest, first, because of the sizable discrepancy previously found to exist between the observed and calculated values for Ce^{3+} in lower symmetry sites; and second, because the simplicity of the electronic configuration and cubic symmetry make the system a facile case for calculations of the mechanisms for producing g-value variations. The search and studies of such compounds are very topical.

Double fluoride crystals with perovskite structure ABF_3 (A = Cs, B = Ca) are very interesting because, on the one hand, they find extensive application in practice, and, on the other hand, they are convenient model systems for studying magneto-optical properties of impurity dopant ions. In principle, it is possible to substitute two various cations in inequivalent positions in these matrices. This enables one to carry out investigations of impurity dopant ions in sixfold or uncommon twelvefold coordination. It is known that the change in the coordination of the dopant ion leads to the essential reconstruction of the crystal field and, as a consequence, to the change in the magnetic and optical properties of the impurity ion.

The aim of this investigation is the first experimental study of the impurity paramagnetic center with cubic symmetry formed by the Ce ion in $CsCaF_3$ crystal.

The crystals were grown using the Bridgman-Stockbarger method. The concentration of the impurity ion was 1 w %.

The parameters of the corresponding spin Hamiltonians, the ground states and their wave functions were determined. Structural models of the observed complexes were proposed. The experimental results were analyzed in comparison with those for the same paramagnetic ions in other hosts.

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P 36 Detection of liquids using magnetic resonance imaging in low-fields

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The problem of security in crowded places is a topical problem to date. The main issue when solving this problem is to detect the dangerous objects in good time and to take every conceivable precaution. However, liquid explosive compounds, which can be prepared in advance or directly before using from corresponding reagents, have been used nowadays as well. Therefore the elaboration of the methods of the operative determination of the type of the liquid is a current problem.

The method of nuclear magnetic resonance is widely used for studying the liquid and solid compounds [1]. The attractiveness of low magnetic fields for solving this problem is in the low cost of the devices themselves and of their operation, and the relatively low energy inputs for the maintenance of the magnetic field.

In this work, it was shown that it is possible to elaborate the methodology of the differentiation of liquid compounds by the magnetic resonance images in low magnetic fields. The most reliable determination of the type of the unknown liquid is possible, when its three parameters are measured: longitudinal and transverse relaxation times, and the self-diffusion coefficient. These parameters can be measured directly in low and ultra-low magnetic fields. On the basis of the above study, it is possible to state that the methodology of the detection of liquid explosive and hazardous compounds using NMR in low and ultra-low fields can be elaborated and successfully introduced for providing security in crowded places.

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P 37 On the structure of the paramagnetic centers in fluorite-type crystals doped with rare-earth ions

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In this work we continue the study by cw EPR of the local structure of the mixed crystals $(MeF_2)_{1-x-y}(RF_3)_y(REF_3)_x$ (where Me = Ca, Ba, Sr; R = Y, La and RE – are the paramagnetic rare-earth ions Ce, Nd, Sm, Er,…) we have been carrying out recent years (see [1] and references therein). These crystals keep the structure of the fluorite CaF_2 up to the value of $x + y \cong 0.4$. But distinct EPR signals are detected only in the samples with relatively low concentrations of R and RE "impurities": $x + y \leq 2$ %.

At $x + y \leq 0.1$ %, the EPR spectra are relatively simple and ascribed to the paramagnetic centers which local structure is very well known (see [2, 3], for example). Changes in the crystal growth conditions (loading of NaF containing salts, growth in the oxygen environment, etc) can lead to the formation of "new" paramagnetic centers which nature is still under discussion. The EPR spectra become even more complicated with the x and y increase due to the additional local clusterization of two and more impurity ions.

Kazanskii [4] hypothesized that the clusterization starts from the very low total concentrations of $x + y \approx 10^{-3}$ by the formation of cuboctahedral clusters $R_6F_{36\ (37)}$. However, in a number of the following works it was shown that such clusterization scheme is not universal and, therefore, the studies of possible models of paramagnetic clusters in fluorite type structures should be continued.

EPR investigation of $CaF_2{:}Sm^{3+}$ was carried out. Only type II of the tetragonal centers reported in literature (type I: $g_{||} = 0.907$ and $g_{\perp} = 0.544$; type II: $g_{||} \approx 0$ and $g_{\perp} = 0.823$) were detected in our experiments.

We have also examined the system CaF_2: Er^{3+}. In the sample with a high concentration of Er^{3+} (0.8 *wt.* %) an intensive EPR spectrum due to the cubic center with g = 6.785 and significantly weaker EPR spectrum of the tetragonal symmetry with $g_{||} = 7.76$ and $g_{\perp} = 6.25$ were observed. In addition to the above mentioned centers, in two samples of nominally pure CaF_2 (with very low impurities concentrations) a tetragonal center with $g_{||} = 1.746$ and $g_{\perp} = 9.16$ was observed while the relative concentrations of three paramagnetic centers in these samples were different.

The obtained results allow refining the models of the impurity paramagnetic centers in fluorites.

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P 38 Identification of impurities in a semiconductor material by means of high-frequency EPR/ENDOR spectroscopy

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Theoretical prediction of a high Curie temperature in ZnO doped with Mn, Co, Fe, and other transition metals has stimulated the investigation of these materials by many research groups. Although charge-compensated Fe^{3+} centers in ZnO:Fe have been observed by means of EPR and have been known for decades, conclusions on the chemical nature of these defects are still contradictory. Originally, these centers were treated as Fe^{3+}-Li^{+} complexes with both ions occupying adjacent cationic position [1]. Recently, however, the centers were interpreted as a substitutional Fe^{3+} ion with a vacancy at an adjacent zinc or oxygen site (Fe-V_{Zn} or Fe-V_O) [2]. In order to conclusively determine the chemical nature of these complexes, electron-nuclear double resonance (ENDOR) spectroscopy was used in the present work [3].

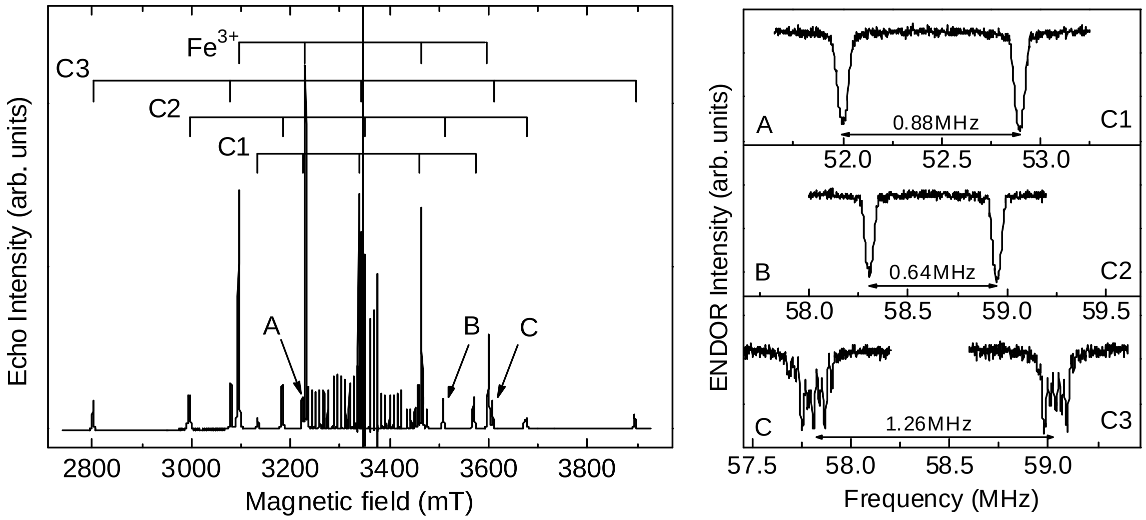

Fig.1. (left) EPR spectrum of a ZnO single crystal for B || *c*. $T = 20$ K, $f \sim 93.9$ GHz. The 30 lines near $g \sim 2$ originate from Mn^{2+}. Three fine-structure quintets originating from the charge-compensated Fe^{3+} centers are indicated. (right) ENDOR transitions of the ^{7}Li nuclei recorded in the 1/2 ↔ 3/2 EPR transitions of the three charge-compensated Fe^{3+} centers.

Fig.1 (left) shows the EPR spectrum of a hydrothermally grown ZnO crystal for B || *c*. Fifteen EPR lines are grouped into three fine-structure quintets originating from three types of charge-compensated Fe^{3+} centers (labeled C1, C2 and C3). Fig.1 (right) shows three ENDOR spectra recorded on the 1/2 ↔ 3/2 EPR transitions of each center. The ENDOR spectra reveal transitions corresponding to a nucleus with $g_N = 2.171$ and spin $I = 3/2$. This unambiguously shows presence of Li as a charge compensator. Depending on the relative positions of the two impurity ions in the hexagonal lattice, three kinds of Fe^{3+}-Li^{+} complexes are formed.

As seen in Fig.1 (right), the hyperfine and quadrupole interactions strongly depend on the particular arrangement of the Fe-Li complex. The electric field gradients at the ^{7}Li nuclei were estimated to be at least 5 times lower than at undistorted Zn sites.

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P 39 Static magnetic susceptibility of Kondo lattice compounds $YbRh_2Si_2$ and $YbIr_2Si_2$

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The static magnetic susceptibility of the heavy fermion compounds $YbRh_2Si_2$ and $YbIr_2Si_2$ is studied starting from the local properties of Yb-ions in a crystal electric field (CEF) on the basis of molecular field approximation and “poor man’s scaling” approach. The molecular field approximation extended to the CEF excited states results in a Curie-Weiss law and Van-Vleck susceptibilities. The Kondo effect leads to renormalization of Curie and Weiss constants converting them to temperature dependent parameters. Our results are well consistent with the experimental data on $YbRh_2Si_2$ and $YbIr_2Si_2$ [1-3] (some of our results were published in [4-6]).

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P 40 Paramagnon excitations theory for magnetic properties of layered copper oxide superconductors

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Using a relaxation function theory we obtain and analyze the dynamic spin susceptibility expressions for doped S=1/2 two-dimensional Heisenberg antiferromagnetic (AF) model in the paramagnetic phase taking into account the thermal damping effects of spin wave-like (paramagnon) excitations. The relaxation function theory is widely applicable for describing the properties of nonequilibrium systems and by itself the Markovian situation can be valid even in the absence of any picture of the system in terms of well-defined excitations [1]. The presentation is valid for all wave vectors throughout the Brillouin zone.

The role of damping (lifetime) of paramagnon excitations, its evolution with doping and temperature, is highlighted in view of magnetic response of high-T_c layered cuprates. It is shown [2] that the theory is able to explain the main experimentally observed features in the imaginary part of the dynamic spin susceptibility in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ as obtained by resonant inelastic X-ray scattering (RIXS) [3] (Fig. 1) and nuclear spin-lattice relaxation rates $1/T_1$ [4] data from pure AF insulator right up to optimally doped high-T_c's in the normal phase (Fig. 2). We emphasize the importance of short-range AF order, its temperature and doping dependence, on dynamic spin susceptibility for magnetic properties of layered copper oxide superconductors.

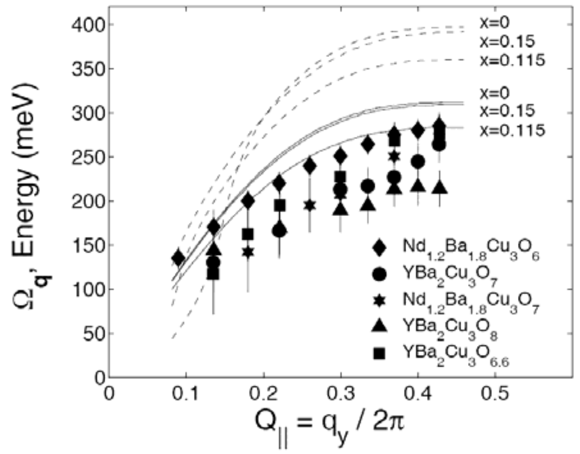

Fig. 1. Dispersion of paramagnon-like excitations along the (0,0)-(π,0) axis as obtained by RIXS. Experimental data at T = 15 K are taken from [4]. Solid lines show calculations with damping of paramagnon-like excitations. Dashed lines show calculations results without damping.

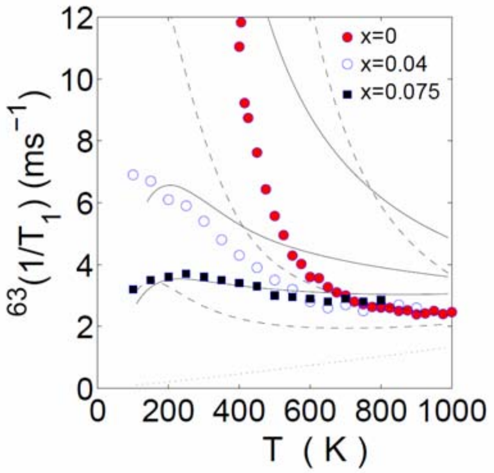

Fig. 2. Plane copper nuclear spin-lattice relaxation rate $^{63}(1/T_1)$ from [4]. Solid lines show calculations with damping of paramagnon excitations. Dashed lines show calculations results without damping. Dotted line show the spin diffusive contribution for x=0.075.

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P 41 Theory for the Gaussian component of the ^{63}Cu nuclear spin-echo decay rate $1/T_{2G}$ in $La_{2-x}Sr_xCuO_4$

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Measurements of the transverse relaxation rates $1/T_2$ in High Temperature Superconductors (high-T_c) provide important information concerning the static spin susceptibility $\chi_{\mathbf{k}}$, which is complementary to the information obtained from nuclear spin-lattice relaxation rate $1/T_1$ [1,2]. The analytical expression for $\chi_{\mathbf{k}}$ [3-5] has similar structure at any doping level as in the isotropic spin-wave theory and is related to antiferromagnetic (AF) correlation length ξ. The temperature dependence of $1/T_{2G}$ is fully described by the temperature dependence of $\chi_{\mathbf{k}}$. Fig. 1 shows the calculated temperature and doping dependences of the Gaussian component of the ^{63}Cu nuclear spin-echo decay rate $1/T_{2G}$ without adjustable parameters. We found that $1/T_{2G}$ increases monotonously with decreasing temperature in agreement with experimental data [2,6-8], opposite to plane copper $1/T_1$.

In high-T_c cuprates the AF correlations are very strong and this leads to necessity of some scaling relation analysis that relates the temperature dependencies of magnetic quantities with that of AF correlation length ξ and the characteristic energy of the AF spin fluctuations ω_{sf}. Both these quantities are related through the dynamical exponent z as $\omega_{sf} \propto \xi^{-z}$. It is known that $\chi(Q=(\pi,\pi)) \propto \xi^2$. Most experiments on high-T_c materials show $z=1$ [2,6-8]. At the quantum critical point $z=1$ is expected while $z=2$ is believed for AF spin fluctuations in itinerant electron systems. However Keren *et al.* [9] showed that dynamical fluctuations of copper nuclei including both spin-lattice and flip-flop processes in the analysis of nuclear magnetic resonance transverse relaxation data gives $z=1$. Both AF x=0 and doped cases showed that $1/T_{2G}$ data are consistent with $z=1$.

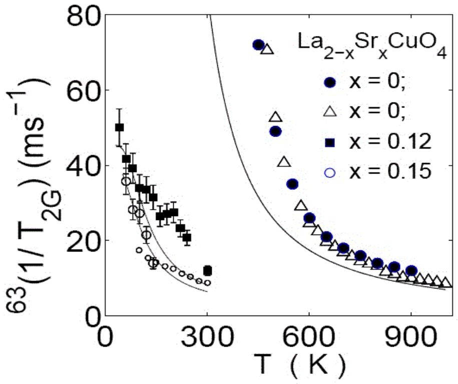

Fig. 1. Temperature dependence of the Gaussian component of the ^{63}Cu nuclear spin-echo decay rate $1/T_{2G}$ for carrier free La_2CuO_4 from Ref. [6] (filled circles) and Ref. [7] (open triangles), and for doped $La_{2-x}Sr_xCuO_4$ (filled squares for x=0.12 and open circles for x =0.15) from Ref. [2]. Small open circles without error bars show the results of Ref. [8] for x =0.15. Lower and upper solid lines show results of the calculations for x =0.12 and for x =0.15, respectively.

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P 42 Analysis of the structure of trigonal center of ion Yb^{3+} in $CsCaF_3$

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A trigonal Yb^{3+} paramagnetic center (PC) in the $CsCaF_3$ single crystal was additionally studied by magnetic resonance and optical spectroscopy methods in paper [1]. The empirical energy level scheme was established and the crystal field (CF) parameters were determined. The CF parameters were used to analyze the lattice distortions in the vicinity of Yb^{3+}. The structure of the PC was found with employment of the fluorites' superposition model (SM) parameters [2]. It is likely that the proposed structure is not plausible because the axial CF parameters (B_k^q with $q = 0$) calculated in the framework of SM differ noticeably from the experimental values. Furthermore, the second coordination sphere of the PC, namely the cube of Cs^+ ions, with one vacancy to implement the local compensation of the excess charge, does not suffer any modifications. The investigation of the analogous center of the Yb^{3+} ion in isomorphic $KMgF_3$ crystal [3] has shown that the absence of one ion in the cube of K^+ ions leads not only to reconstruction of nearest sphere but also to substantial changes in positions of ions of the other coordination spheres.

In this paper more detailed analysis of the structure of T_{trig} was been realized. It was demonstrated that satisfactory results may be obtained within the framework of the SM, taking in consideration not only the first coordination sphere of F^- ions, but also the second sphere of Cs^+ ions. It was found that three F^- ions of the nearest surrounding octahedron, placed symmetrically along the threefold axis on the side of the vacancy, upon the formation of T_{trig} in $CsCaF_3$ move away from the Yb^{3+} ion and deviate appreciably from the PC axis. The second group of three F^- ions, on the contrary, comes nearer to the impurity paramagnetic ion (PI), and moves to the PC axis. Three Cs^+ ions of the second cube coordination on the side of the vacancy, come slightly nearer to the Yb^{3+} ion, and substantially move to the PC axis. The second group of three Cs^+ ions, from the side opposite to the vacancy, also comes nearer to the Yb^{3+} ion and slightly moves to the PC axis. Cs^+ ion, placed on the threefold axis, comes noticeably nearer to the PI when forming T_{trig}. Theoretical CF parameters calculated within the framework of the proposed PC structure correspond to the experimental values very well.

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P 43 Superoxide- and NO-dependent mechanisms of reprogramming of bone marrow cells by tumor cells

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Introduction. Changes in the mitochondrial redox state of tumor cells cause reprogramming of iron metabolism, contributing to the iron accumulation in the tumor microenvironment. Activation of the superoxide generating systems of neutrophils and mitochondria in the bone marrow (BM) by using the “free” iron - labile iron pools (LIP) - is a redox-dependent mechanism that through the regulation of concentrations of matrix metalloproteinases (MMPs) is responsible for the invasion and metastasis of tumor cells.

Aims of the work. To determine the levels of LIP, superoxide generation rates, the rates of NO generation and the activity of MMP-2 and MMP-9 gelatinases in tumor tissue and BM of rats with Guerin carcinoma before and after their contact incubation; to compare the results with those obtained from the healthy donors and patients with breast cancer with and without metastases.

Methods. *EPR, superoxide spin trapping, polyacrylamide gel zymography*.

Results. Increased levels of LIP, NO, superoxide generation rates and active forms of gelatinases are revealed in the tumor tissues. After the incubation of the tumor tissue with BM cells, the values of the observable parameters increase significantly on the border as well as at a distance from the border line. Appearance of LIP in the extracellular matrix activates the mitochondrial and neutrophils’ superoxide radicals generation systems in BM of intact animals and deepens these processes in BM of animals with tumors. In BM of the breast cancer patients without metastases high (in comparison with the healthy donors’ BM) levels of LIP, superoxide generation rates, MMP-2 and MMP-9 are observed.

Conclusions. High superoxide generation rates, activation of the latent forms of MMP-2 and MMP-9, re-enforcement of the oxidative damage through the direct influence on the BM cells as well as through the reprogramming of the mitochondrial metabolism and Nox activation favor the tumor cells growth and their own metabolism. Abnormal values of LIP, superoxide generation rates and MMPs activity in the tissues of breast cancer patients may indicate the presence of the clinically undetectable distant metastases and become a part of diagnostics and therapeutic treatment.

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P 44 Theory of bimolecular spin exchange between charged free radicals in dilute liquid solutions.

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Kinetic equations for density matrices of the ensembles of charged paramagnetic particles in diluted liquid solutions are obtained. Rate constants of bimolecular spin exchange are calculated numerically. These calculations were performed within model of diffusion passage through a region of exchange interaction that exponentially decays when the distance between spins increases.

The EPR spectra of the water solutions of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidiniloxy (3-carboxy-proxyl, $C_9H_{16}NO_3$) with NaOH and HCl were studied and analyzed using our theoretical calculations.

P 45 Optimization of the protocol for small peptide solution structure refinement using NMR restraints in the bath of explicit water

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NMR spectroscopy is a widely used approach for protein solution structure calculation. However, determination of the conformations for small peptides, which undergo fast molecular motions, remains to be a challenge due to the lack of sufficient number of conformational constraints.

Here we report the novel protocol for small peptide structure refinement using NMR-derived restraints in explicit water environment. The developed algorithm substantially increases quality of structures, in particular Ramachandran plot statistics, and decreases RMSD for back-bone heavy atoms within the family of calculated models. The described protocol can be used for the determination of short peptide solution conformations and for optimization of larger protein models, which contains poorly structured fragments.

P 46 Investigation of NMR spectra of polybutadiens based on DFT method

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It is known that in the industrial synthesis of polybutadienes there is a problem of identifying compounds composition that is required for further use in producing polybutadienes [1]. Allocation of different monomer structures in macromolecule strongly affects many practical properties of the polymer, especially elasticity, toughness, etc., as well as its behavior under extreme conditions, such as at very low or, on the contrary, very high temperatures. NMR spectroscopy is widely used to study the microstructure of polybutadienes. It should be emphasized that the form of the polybutadienes NMR spectrum is very complex and the experimenter is faced with the problem of relating the resonance lines with different monomer units in the polymer. The solution to this problem is possible on the basis of theoretical studies of spatial and electronic structure of polybutadienes using modern quantum chemistry methods, and interrelation of structure with parameters of the NMR spectra.

In this study we calculate the spatial and electronic structure of isolated polymer model fragments in different configurations. Computation of the structures and magnetic shielding constants of proton and carbon nuclei were carried out within the framework of density functional theory (DFT) with functional PBE and 3z basis set by using Priroda program [2]. The calculations of magnetic shielding constants were conducted with DFT method using the gauge-invariant atomic orbitals (GIAO) [3]. Also we calculate the spatial and electronic structure of polymer model fragments in periodic condensed matter with boundary conditions using DFT method in the plane waves basis set realized in VASP [4] program (part of the software package MedeA [5]).We conducted a comparative geometric analysis for isolated molecule and molecule in condensed matter, as well as analysis of changes of magnetic shielding constants for isolated molecule and for molecule in condensed matter.

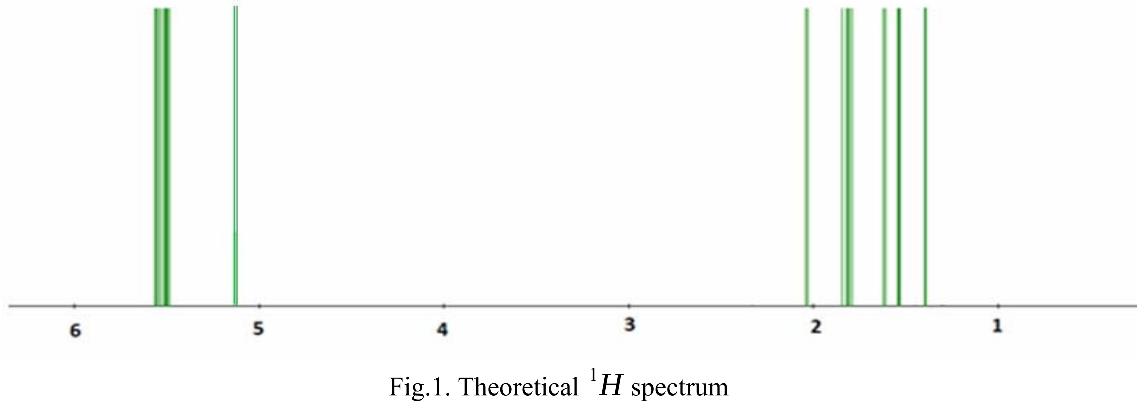

Fig.1. Theoretical ${}^{1}H$ spectrum

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P 47 Diffusion characteristics of Aβ amyloid peptide with various point mutations

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Alzheimer disease is one of the most common reasons of death for elderly people. It brings out torment as for patient himself, so for his relatives, requires expensive care. Until now there is no cure for an Alzheimer disease. When talking about the pathology of disease, it originates from formation of so called amyloid plaques in the brain tissue of the patient [1,2]. Amyloid plaques are formed as a result of defects in the metabolism of proteins, normally responsible for some certain functions in a human body. One of these is APP (Amyloid Precursor Protein), transmembrane protein, catalytic cleavage of which results in formation of so called Aβ-peptide having the size of 37-49 aminoacid [3].

It is necessary to mention that the reason of death is apoptosis of brain neurons, meanwhile last decade researches have shown that amyloid plaques themselves are not responsible for the death of neurons. At the same time there are proofs showing that oligomeric aggregates of Aβ-peptide, having relatively small sizes and high translational mobility, may form ionic channels on the surface of cell membranes, which results in increase of Ca^{2+} concentration inside the cell [4].

The structure of channel forming Aβ aggregates, the details of mechanisms of channel formation, the role of membrane lipid composition and constitution of environment are still not well known.

Current work is dedicated to the study of the role of various point mutations on diffusion characteristic of Aβ-peptide. Obtained self-diffusion coefficients were used to estimate the hydrodynamic radii of Aβ-peptide.

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P 48

Photoinduced effects in EPR spectra of spin-crossover Fe(III) Schiff-base complexes

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Induced by an external influence (temperature, pressure or photoirradiation) transitions between low spin (LS, S=1/2, $t^5_{2q}e^0_q$) and high-spin (HS, S=5/2, $t^3_{2q}e^2_q$) states are possible in the quasi octahedral Fe(III) complexes. The effects of light induced exited spin state trapping (LIESST) and ligand driven light induced spin change (LD-LISC) was discovered on Fe(II) and on Fe(III) complexes [1]. The spin-state photoswitching dynamics spanning ten decades in time is investigated now namely on spin-crossover compound [TPAFe(III)TCC]PF_6 by femtosecond optical spectroscopy [2,3].

The aim of our work is to obtain information on photoswitching dynamic of Fe(III) Schiff-base powder complexes by time-resolved EPR spectroscopy in window $5{\cdot}10^2$-$5{\cdot}10^4$ ns and investigate stationary effects of laser irradiation in wide temperature interval. The complexes [FeSaltenL]$BPhen_4$ with L=Him (only HS state) I and with L=Pic (spin-crossover LS⇔ HS states) II were irradiated by laser (λ=532 nm) in ligand-metal charge transfer (LMCT) band. The following experimental results of EPR investigation (together with optical and magnetic susceptibility measurements) can be selected:

-the common tendency to decrease EPR signals integral intensity under irradiation was observed [4,5]. The time of stationary signal intensity state reach and recovery after laser switching off was 7-10 min. Some retreats from common tendency observed on spin-crossover complex II.

-the effect of change the spin-transition curve (HS fraction vs. temperature) after long photoirradiation has been found for complexes II.

-the studies of powder samples by time-domain EPR (nano- and micro- seconds) demonstrated very high sensitivity of emissive, absorptive spectra, and kinetic parameters to prehistory and preparation conditions of sample. Our data show an emissive signal formed after the laser flash, which coincides in form with the integral continuous-wave EPR spectrum. The time profiles of the emissive signals are characterized by two exponential functions describing the fast and slow kinetics.

The possible interpretation of features observed under laser irradiation contains evaluation the following factors: contribution of temperature, the change of ligands conformation, and photochemical reactions Fe (III) => Fe (II).

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P 49 The scopes and limitations of the GIAO calculations of ^{31}P NMR chemical shifts

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It is well documented today that GIAO approach allows to evaluate ^{1}H/^{13}C/^{15}N NMR chemical shifts (CS) with high accuracy. Its quality is good enough even to discriminate fine structural differences such as conformational, isomeric and tautomeric.

To this end non-empirical method to estimate ^{31}P CSs is also of high necessity because phosphorus is involved in many practically important compounds and its chemical shift depends dramatically on the structure. However, it is still unclear if GIAO method can be reliably used to calculate ^{31}P CSs with reasonable computational costs. In fact, there are only very few reports devoted to ^{31}P NMR CS calculations [1-3].

In this work we analyze the influence of the theory level (involving both steps - geometry optimization and chemical shift calculation) on the quality of the calculated CSs in order to find an optimal theory level which is accurate enough however still applicable to compounds of practical interest. Scopes and limitations of the method are discussed.

We thank Russian Foundation for Basic Research (grant Nos. 13-03-00169-а, 14-03-31952 мол-а) for the support of this work.

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P 50

EPR and optical spectroscopy of ceria powders containing manganese

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Cerium dioxide (CeO_2) is a perspective host material for many applications including such fields as energy, chemistry and medicine [1,2]. The main feature of cerium dioxide is the ability to absorb and release oxygen under oxidizing and reduced conditions. In pure ceria this process is associated with the change in the oxidation state of cerium between Ce^{3+} and Ce^{4+}. The performance of CeO_2-based materials could be improved by the doping with the aliovalent ions. It was found experimentally that manganese added to CeO_2 enhances its redox properties and catalytic oxidation activity. Recently published results of DFT calculations revealed that the manganese doping of CeO_2 promotes the oxidation of Ce^{4+} to Ce^{3+} [3]. The purpose of the present study was to prove this supposition using the cw EPR technique and the optical spectroscopy to study two types of CeO_2 powder containing different amount of manganese.

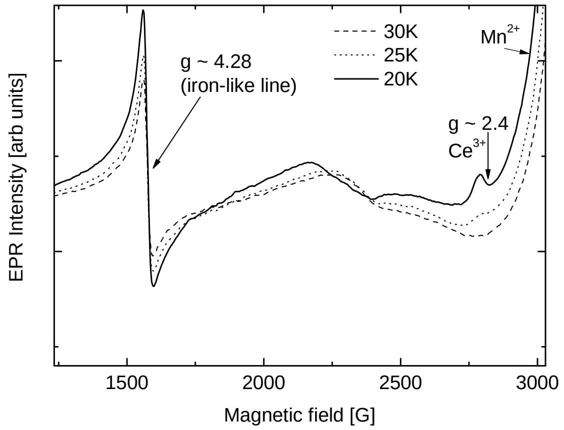

Fig.1. X-band EPR spectra of CeO_2 powder contaminated with manganese ($5.7 \cdot 10^{-3}$ at.%).

EPR measurements were made at ~9.4 GHz and temperatures from 10 K up to 300 K. For the sample with bigger amount of manganese (the concentration ~ $5.7 \cdot 10^{-3}$ at.%) we observed at the temperature 10 K the EPR line with g ~ 2.4 (Fig.1) that we tentatively ascribe to the Ce^{3+} in a trigonal site [4]. The absorption line disappeared at temperatures above 25 K. The photoluminescence measurements supported the presence of F-centres in sample with bigger amount of manganese.

The possible model is discussed in the present work.

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P 51 The study of high viscosity oil and bitumen by EPR

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Due to the great heterogeneity of properties and composition of high viscosity oils from different oilfields, a task to develop the methods of monitoring the characteristics is still of a great importance. Electron paramagnetic resonance (EPR) is known as one of the informative tools for oil research.

Several samples of high viscosity oils from different oilfields of Republic Tatarstan were investigated. Typical EPR spectra of oil are due to the hyperfine structure of vanadyl complex VO^{2+} ($^{51}V^{4+}$, $^{3}d^{1}$, $S = 1/2$, $I = 7/2$, $g_{\parallel} = 1.9640\pm0.0005$, $g_{\perp} = 1.9840\pm0.0005$) and from the single line of carbon free radicals (FR), which is in agreement with results of [1, 2, 3]. Atoms in the vanadyl-porphyrins are arranged practically in a plane defining thus the g-factor and hyperfine A tensor have an axial symmetry [2, 3, 4]. The EPR spectrum of the vanadyl-ions consists of 16 components representing the 2x8 hyperfine patterns for the parallel and the perpendicular complex orientations.

The relative intensities of the spectra of vanadyl-ions and free radicals differ from sample to sample. We have considered the ratio K of vanadyl line integral intensity to FR line integral intensity, this parameter can be used as an indicator of the oxidation of vanadyl-porphyrins because of geological processes.

The temperature dependences of EPR spectra were investigated in temperature range of 300-700K. The particular features of dependences of different samples allow to suggest the simple method of the oil viscosity estimation.

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P 52 Nuclear-electron magnetic resonance in solid state antiferromagnets

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Magnetic (spin) superfluidity is a magnetic analog of superfluidity and superconductivity. In contradistinction from superfluidity (discovered by P.L. Kapitza in 1938) and superconductivity (discovered by Kamerlingh Onnes in 1911), where mass and charge flow without friction, in magnetic superfluidity magnetic moment (magnetization) flows without dissipation. Superfluidity is the main dynamical property of the Bose-Einstein condensation (BEC), which can be described as a quantum transport phenomenon emerging in the presence of BEC wavefunction gradients. The effect of magnon BEC was observed experimentally in superfluid ^{3}He-B in 1984 [1,2]. It has been predicted, that the same phenomena should exist in solid state antiferromagnets with coupled nuclear-electron precession [3]. The predictions were successfully confirmed [4,5]. Here we present the results of further investigations on the BEC of elementary magnetic excitations – magnons – in antiferromagnets with a dynamical frequency shift. The development of new techniques and the search of more homogeneous samples are the aim of the current work. New results will be reported.

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P 53 Reduction of helium-3 relaxation times at high magnetic fields

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Recent developments of hyperpolarised noble gases applications attract an additional interest to various polarisation methods [1-3]. One of the well-known but rarely used way to polarise helium-3 is the “brute force” method that requires implementation of very low temperatures and high magnetic fields [4]. It allows to achieve high levels of polarisation but in expense of the polarisation duration of many hours due to long T_1 relaxation times at experimental conditions.

An application of moderate temperatures and magnetic fields (2.4 K and 8 T) successfully allows to use polarised helium-3 with enhanced magnetization magnitude in lung imaging experiments at room temperatures [5]. However, the duration of the polarisation process still takes many minutes. This fact sets certain limits on the gas quantities for this polarisation technique. Reduction of helium-3 T_1 relaxation times during polarisation process to orders of milliseconds (or shorter) can significantly improve efficiency of this method.

Previous investigations of PrF_3 powder samples and its influence on ^{3}He relaxation at low magnetic fields [6] show the potential of these samples as a material for helium-3 T_1 relaxation times reduction at high magnetic fields.

In this work synthesized powder of PrF_3 nanoscaled particles was used as a sample. Series of NMR experiments on ^{3}He gas T_1 relaxation in the experimental cell containing a sample are carried out on a home built set up at various magnetic fields up to 5 T and at liquid helium temperature. Current progress of this work will be reported.

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P 54

Low-field NMR method for determination of fat, protein and moisture in food powders

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The measurement of parameters such as fat, protein and moisture content is important to help define the nutritional value and quality for many foodstuffs and agriculture products. ISO LFNMR standards for food products are based on measurement of FID and echo at a strictly fixed times and need the reference samples. Much useful information which is contained in the full NMR signals is lost. Measurement and joint processing of full FID and CPMG signals allows one to define the fuller component composition of most foods. Analytical technique is proposed, in which the determination of fat, moisture and protein content in food and feed powders is carried out by NMR relaxation method. Determining the true intensities of the corresponding components of relaxation by complete fitting of FID signal is based on semi-empirical model:

$$I(t) = A_{p0} \cdot \{(1 - f_g) \cdot \exp[(-t/T_{2pa})^2] \cdot \sin(bt)/(bt) + f_g \cdot \exp[(-t/T_{2pg})^2]\} +$$
$$+ A_{w0} \cdot \exp(-t/T_{2w}) + A_{f0} \cdot \exp(-t/T_{2f}) \cdot \exp[(-t/T_{2w})^2]$$

Overlapping water signal and magnetic field inhomogeneity complicate determination of the fitting parameters of fat components with long T_{2f} (and T_{1f}). The true form of fat components of FID can be determined by removing moisture from the sample (Fig.1a) or eliminating overlapping the signals of water and protein using the protocol: (90°*FID1* … 1,5T_{1f} … 90° *FID2* ... 5T_{1f} ...)$_N$, where N is the number of accumulations. Signals of protein and water (with short T_1) after second 90° pulse (FID2) remain the same as in FID1, while the fat's signal is partially suppressed. As a result, the difference (FID1-FID2) contains only fat component (Fig.1b,c) and T_{2f} and T_{2fv} in eq.1 can be determined. Accurate amplitude of fat component A_{f0} is determined by CPMG method. Then T_{2fat} and A_{f0} is used to complete fitting of FID1.

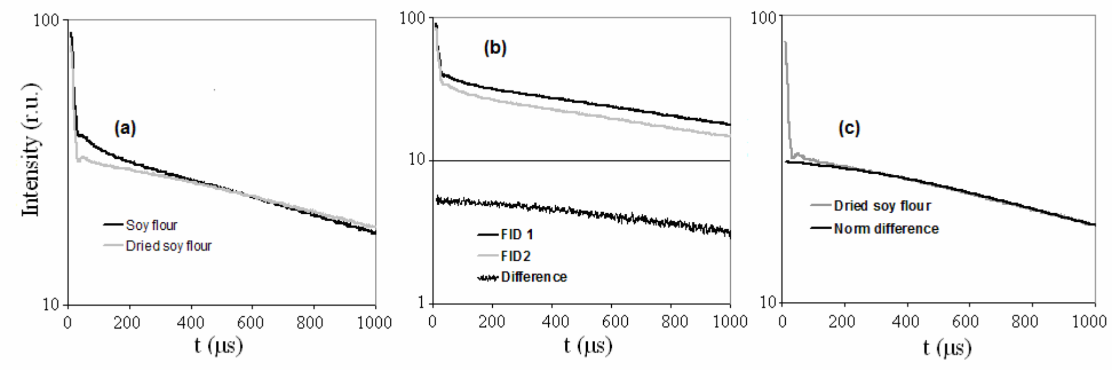

Fig.1.

Software package for recording and consistent mathematical treatment of FID and CPMG curves was developed as a new interface for NMR - analyzer "Hromatek-Proton-20M".

P 55 Crystal field and magnetic properties of the EuF_3 Van-Vleck paramagnet

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We report on results of the crystal filed analysis and magnetic properties of the Van-Vleck paramagnet EuF_3 having the orthorhombic crystal structure *Pnma* (62) studied by ^{19}F NMR in powder samples. The crystal field at Eu^{3+} position, spectra of electronic excitations of the Eu^{3+} ions and magnetic interactions between the rare-earth and fluorine ions have been on the focus of the study.

The set of crystal field parameters for the Eu^{3+} ions with the C_S point symmetry in EuF_3 has been estimated using the semi-phenomenological exchange charge model, and then corrected by comparing the results of calculations of crystal field energies with the experimental data.

Transitions of the 4f-electrons to excited states and back to the ground state give rise to fluctuations of the Eu^{3+} magnetic moment. These fluctuations affect the NMR spectrum and nuclear relaxation of ^{19}F through the dipole-dipole and the transferred hyperfine interactions. The ^{19}F NMR spectra were measured in EuF_3 powders in the static magnetic field B_0 = 5965 G at the NMR frequency of 23.9 MHz. The NMR spectra taken at temperatures 4.2 K, 77 K and 300 K were recovered by the Fourier transform of the spin-echo patterns. The ^{19}F NMR line was found very narrow (~10 G at 4.2 K and ~7 G at 300 K). This suggests that the dipole and transferred hyperfine magnetic fields induced by the Eu^{3+} ions are negligible because the Eu^{3+} ions are mainly in the ground nonmagnetic state $^7F_0$ at low temperatures, and at T = 300 K these fields are averaged to zero due to very fast fluctuations of the Eu^{3+} magnetic moments.

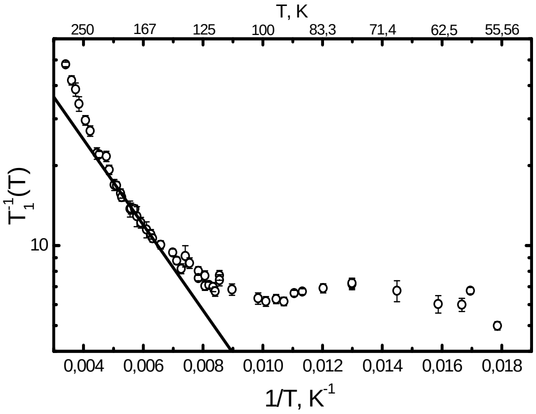

Fig.1. ^{19}F NSLR rate vs. 1/T in EuF_3

Temperature dependencies of ^{19}F nuclear spin-lattice relaxation (NSLR) rates in the EuF_3 powder samples were measured in the temperature range 55 – 300 K. For Eu^{3+} ion in EuF_3, the energy gap between the ground and the first excided states is ~370 K. Therefore, excited 4f electrons of Eu^{3+} ion can induce the fluctuating magnetic fields at the ^{19}F nuclei only at rather high temperatures. It is seen in Fig.1 that the T_1^{-1}(T) increases rapidly at temperatures $T > 110$ K. Values of $1/T_1$ have been found in the range from 5 to 50 s^{-1}, i.e. the ^{19}F nuclear spin-lattice relaxation is rather slow as compared to relaxation rates in other Van Vleck paramagnets. We suggest that the increase of T_1^{-1}(T) in the temperature range 110 – 300 K is determined by weak fluctuations of local magnetic fields induced by Eu^{3+} magnetic moments. Solid line in Fig.1 corresponds to the function $T_1^{-1} \sim \exp(-\Delta_1/T)$ with $\Delta_1 = 370$ K. One can see that the ^{19}F NSLR in EuF_3 is not explained only by the thermal excitations of the Eu^{3+} ions to the lowest excited crystal field level. Most likely the influence of other excited levels should be taken into account. Other mechanisms of ^{19}F NSLR in EuF_3 will be discussed.

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P 56 Electron spin resonance in $Yb(Rh_{0.73}Co_{0.27})_2Si_2$ below 1 K

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We report Electron Spin Resonance (ESR) experiments on the heavy-fermion metal $Yb(Rh_{0.73}Co_{0.27})_2Si_2$ in the temperature range $0.75\ K \leq T \leq 4\ K$. The ESR measurements were performed at X-band frequencies using a home-built ^3He cryostat. We found that below 1.3 K the ESR spectra of $Yb(Rh_{0.73}Co_{0.27})_2Si_2$ split into two lines. Such a behavior can be explained by the strong anisotropy of the ferromagnetic ground state in agreement with magnetization measurements [1].

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P 57 Investigations of $(CaCu_3Ti_4O_{12})_{1-x}(SrFe_{12}O_{19})_x$ systems by ESR

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Materials with high dielectric constant attract attention because of their practical application in microelectronics, capacitors or memory elements. Among the materials with giant values of the effective dielectric constant ε, there is CaCu (CCTO) and related materials. Ceramics $CaCu_3Ti_4O_{12}$ (CCTO) belongs to the family type $ACu_3Ti_4O_{12}$ (where A = Ca or Cd) [1]. Their advantage is that, not being a ferroelectric, they have constant and very high values of the effective ε ~ 10^4-10^5 in wide temperature (100-600K) and frequency ranges (up to 10 MHz) [2, 3]. Unusual dielectric properties of CCTO accepted to discuss the model of grain-boundary when the interlayer polarization was observed according to Maxwell-Wagner in an inhomogeneous dielectric medium [2-4].

Electron spin resonance (ESR) measurements were performed in $CaCu_3Ti_4O_{12}$, $(CaCu_3Ti_4O_{12})_{0.9}(SrFe_{12}O_{19})_{0.1}$ in X- and Q-bands at 300 K. The ESR spectrum in ceramics consists of one exchange-narrowed line with the g-factor about g~2.14. The ESR spectra of these compounds are presented in Figure 1. The analysis of the ESR spectra allowed to estimate linewidth ΔH =220 Oe for pure ceramic $CaCu_3Ti_4O_{12}$; ΔH =640 Oe and 830 Oe for doped with 10% of strontium hexaferrite $SrFe_{12}O_{19}$ at X- and Q- band relatively. The reasons for the broadening of ESR lines in the Q-band are discussed.

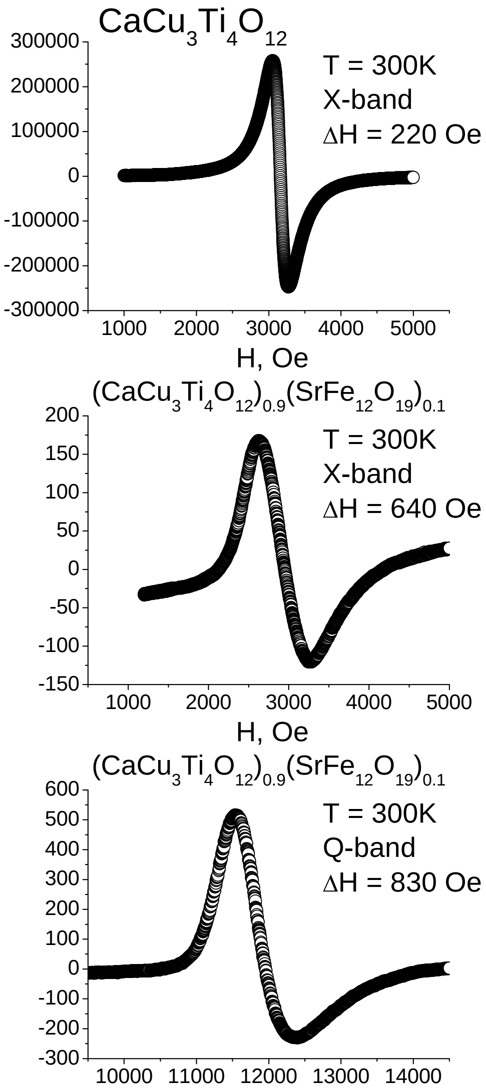

Fig.1. ESR spectra of $(CaCu_3Ti_4O_{12})_{1-x}(SrFe_{12}O_{19})_x$.

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P 58 Growth and spectral properties of solid solutions with colquiriite structure $LiCa_{1-X}Sr_XAlF_6$:Ce^{3+}

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Fluoride crystals with the colquiriite structure activated by the corresponding ions are effective active media of solid-state lasers [1]. The advantages of these compounds over oxide crystals - the melting point is significantly lower and band gap is much wider. Significant inhomogeneous broadening of the vibrational laser transitions of these ions causes a broad band lasing restructuring, as well as the ability to generate ultrashort pulses [2].

The aim of this work is experiments on growing new materials based on fluoride crystals with the colquiriite structure with composition $LiMeAlF_6$ (Me = Ca, Sr) and their solid solutions, as well as the study of their optical properties.

As a result of experiments parameters of the process of growing crystals of solid solutions of $LiCa_{1-x}Sr_xAlF_6$ were established, providing high quality of the crystallized material. X-ray diffraction measurements have shown that the synthesized crystals of $LiCa_{1-x}Sr_xAlF_6$ series with a variable ratio component SrF_2 and CaF_2 single crystals have single phase of colquiriite structure.

Studies by optical spectroscopy revealed three optically inequivalent Ce^{3+} impurity ions centers in $LiCa_{1-x}Sr_xAlF_6$ crystals. In comparison with the crystal $LiCaAlF_6$: Ce^{3+}, for $LiCa_{0,2}Sr_{0,8}AlF_6$: Ce^{3+} crystal shorter wavelength centers have a broader luminescence band (275 - 320 nm) and there is larger value of relative luminescence intensity for these centers. Another important result is larger absorption coefficient of Ce^{3+} ions in $LiCa_{0,2}Sr_{0,8}AlF_6$: Ce^{3+} crystal (20 cm^{-1} at 270 nm) compared with the crystal $LiCaAlF_6$ (6 cm^{-1} at 270 nm) with the same amount of CeF_3 charge in the melt (1 at. %). It is obvious that in the crystal of the solid solution a redistribution of impurity centers was produced towards the formation of shorter wavelength center, thus increasing the distribution coefficient of the impurity in the crystals.

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P 59 The EPR method in studying of mineral-geochemical features of profile zones of ancient weathering crust of the Volga-Ural area

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Within the Volga-Ural region ancient (pre-Devonian) weathering crust is developed on the rocks of the crystalline basement (average depth of 1600-1800 m) and are blocked by deposits of a sedimentary cover. Study of the weathering crust was carried out on a core material of wells of deep drilling. The studied rocks of the weathering crust belong to morphological areal type and are characterized by an aeration profile with development of several zones from the bottom up. For example, zones of disintegration, hydration and leaching are allocated in well №34 [1].

The object of this work is studying of mineral-geochemical features of ancient weathering crust with EPR method. First of all initial rocks were investigated with the EPR method, then rocks were divided into fine (sandy) and clay fractions which were analyzed before the isothermal annealing of rocks was carried out and after it. The measurements were carried out on a X-band spectrometer PS-100X (ADANI, Minsk) at room temperature. The thermal annealing of rocks samples was carried out at 1200°C in a quartz tube.

Kaolinite is the typical mineral of the hydration and leaching zone of a weathering crust profile, it is an indicator of intensively weathered rock. In EPR spectra kaolinite is identified by Fe^{3+} entering the structure of a clay mineral and giving EPR signals at $g \sim 4$, the wide line at $g \sim 2$ of iron oxides and hydroxides, and also by radiation and thermal stability of radiationally-induced $Si\text{-}O^{-}\text{-}Si$ centers [2]. Considering its thermal stability at 350°C, the ion-radical R with parameters g{2.0486; 2.0083; 2.0011} can be referred to the radical O^{-} of the $Si\text{-}O^{-}\text{-}Si$ center in kaolinite.

Presence of Mn^{2+} ion in the lower part of a weathering crust profile – in a disintegration zone – is an indicator of carbonates migration on an aeration profile from the top horizons.

The E' center of quartz, the steadiest mineral of a profile, is observed in the hydration and leaching zone. In the disintegration zone it is fixed poorly because of a small concentration of quartz in this zone. After annealing at 350°C a symmetric line of E"-center in quartz is observed testifying its generation by α-ionizing radiation [3]. Concentration of E"-centers decreases with depth growth on a profile from the hydration and leaching zone to the disintegration zone. It is connected with features of a profile formation and mineral weathering rate or decrease in a dose of a paleoradiation.

Results of research based on EPR method confirm the mineral-geochemical model of formation of a zoned profile of weathering process. The hydration and leaching zones differ by increase of clay content and the content of kaolinite concerning other clay minerals. Weathering process causes transformation of clay minerals, the final product is kaolinite.

This work was funded by the subsidy of the Russian Government to support the Program of competitive growth of Kazan Federal University among world class academic centers and universities.

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P 60 An application of immobilized Vaska's complex for generation of PHIP in a gas-phase hydrogenation

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The methods increasing population differences of nuclear spin energy levels are increasingly being used to enhance the sensitivity of NMR and MRI. Parahydrogen induced polarization (PHIP) is one of these methods. PHIP can provide enhancement of NMR signals up to 4-5 orders of magnitude [1]. Necessary condition of PHIP observation is the pairwise addition of two atoms of parahydrogen. By these reason, catalysts which fulfil interaction with parahydrogen is key in generating PHIP. Since pairwise manner of H_2 addition is a characteristic feature of many catalytic systems based on transition metal complexes, commonly, PHIP is produced in homogeneous hydrogenations using solutions of transition metal complexes as catalysts [2]. However, a major disadvantage of the homogeneous catalysts is the difficulty in separation of the dissolved catalyst from the reaction mixture, which sets restrictions for PHIP application in studies of biological objects, for instance. It is a fact that heterogeneous catalysts can be easily removed from the reaction mixture. Therefore, the use of immobilized transition metal complexes as catalyst is a promising approach for generating PHIP, because most probably the homogeneous hydrogenation reaction mechanism will be preserved after the immobilization.

Recently, it was shown that application of immobilized rhodium complexes allowed detecting PHIP [3]. However, our studies have shown that immobilized rhodium complexes are not stable in reaction conditions and is rapidly reduced [4]. In present work, we studied the possibility of generating PHIP in gas-phase hydrogenation of small organic molecules (propene, propyne and 1-butyne) with the use immobilized iridium complex which was prepared from Vaska's complex ($Ir(CO)(PPh_3)_2Cl$) covalently grafted on phosphine-modified silica gel (PPh_2-$(CH_2)_2$-$[SiO_2]_n$). It was found that the gas-phase hydrogenation of a triple carbon-carbon bond (propyne, 1-butyne) leads to a significant PHIP-enhancement of NMR signals (200-300 times) corresponding to protons of vinyl fragments under both PASADENA and ALTADENA conditions. At the same time, in the case of hydrogenation of a double bond (propene), only a weak PHIP signal enhancement was found. The investigation of the immobilized catalyst which was tested at temperatures of up to 140 ^{o}C has shown that in comparison with immobilized rhodium complex the immobilized Vaska's complex is more stable and is not reduced. Nevertheless, eventually at storage in inert atmosphere the immobilized complex is destroyed. This leads to decrease of enhancement of NMR signals and increase of catalytic activity. The reasons of such interesting finding are discussed.

This work was supported by the grants from RFBR (12-03-00403-a), the Council on Grants of the President of the Russian Federation (MK-1329.2014.3), the program of support of leading scientific schools (NSh-2429.2012.3), the program of the Russian Government to support leading scientists (11.G34.31.0045).

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P 61 Conformational analysis of P,N-containing eight-membered heterocycles and its Pt complexes in solution

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Investigations toward effective energy technologies are focused on the interconversion of chemical and electrical energy. An attractive option is to store the energy in the form of fuels with a high energy density, such as H_2. This necessitates efficient catalysts for both the production and the utilization of hydrogen. Therefore a great efforts have been directed to design molecular catalysts that employ cheap and abundant metals. Efforts have focused on developing first-row metal complexes that contain an amine base in the second coordination sphere. In these complexes the base facilitates the heterolytic cleavage/formation of the H−H bond and functions as a proton relay.

In this context metal complexes based on P,N-containing heterocycles are of interest - the cyclic diphosphine ligand $P^R{}_2N^R{}_2$ (P_2N_2 stands for a 1,5-R′-3,7-R derivative of 1,5-diaza-3,7-diphosphacyclooctane) contains soft coordination sites that allow getting variety of metal complexes. Thus a series of $[Ni(P^R2N^{R'}2)2]^{2+}$ catalysts were developed for H_2 oxidation or production. In the series of experimental and theoretical mechanistic studies authors investigated different factors that influence function of this types of complexes [1, 2, 3]. It was also revealed that catalytical activity depends also on conformational kinetics: *viz* the rate-limiting stage is intramolecular proton transfer due to **CB-CW** interconversion. However, there is only very few papers dealing with analysis of intramolecular kinetics of such complexes, particular, in solution [4, 5, 6].

In this work we tried to reveal key factors that control conformational equilibrium and dynamics of these heterocycles and their Pt complexes. Firstly, we analyzed the influence of substituents at P and N atoms on conformational characteristic of eight member ring itself. Secondly, dependence on substituents for Pt complexes was considered. Finally, difference of bis *versus* mono ligand complex was analyzed. Theoretical finding were checked experimentally in solution by DNMR.

We thank Russian Foundation for Basic Research (grant Nos. 13-03-00169-a, 14-03-31952 мол-а) for the support of this work.

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P 62 EPR investigations of two SMMs built of 3d-4f ions

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In recent years a study of single molecule magnets (SMMs) [1] attracted much attention. The main problem of SMMs chemistry is the creation of SMMs that would exist at higher temperatures (50 - 100 K). For this purpose it is necessary to use the orbital-degenerate magnetic centers (ions with unfilled f-and d-shells), in which the spin-spin interaction is strongly anisotropic.

We have found that the compounds $Fe_2Dy_2(OH)_2(\text{tritehanolamine})_2(O_2C_7H_4\text{-meta-}CN)_6$(I) and $Fe_2Dy_2(OH)_2(\text{teaH})_2(p\text{-}CH_3\text{-}C_6H_4COO)_6$(II)have the SMMs properties. These SMMs are tetranuclear clusters built of iron and dysprosium ions and have different blocking temperature magnetization.

EPR spectra were measured in X- and Q-bands at low temperature (4 - 15K). The analysis of the spectra was performed using simulations of EPR spectra.

The EPR spectra are observed from dimer of dysprosium ions at low temperature (T<15K) for both SMMs. The shape of the EPR spectrum in Q-band changes after the compound is subjected to the effect of the external magnetic field. This change can be described by the appearance of some ordering as it indicates that the number of clusters with g_z oriented along external magnetic field increases after the effect of the external magnetic field. This effect was observed for both SMMs.

We are grateful to the Russian Foundation for Basic Research № 13-02-01157 for partial financial support.

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P 63 Nuclear magnetic resonance in a chiral helimagnets

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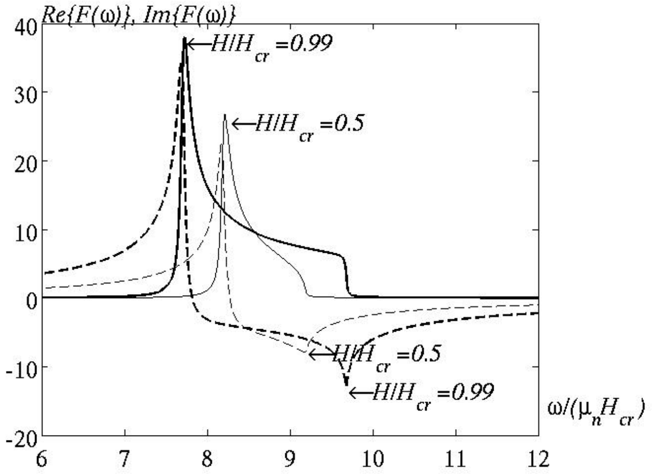
Currently, considerable attention is paid to investigations of magnets with inhomogeneous ground state and, in particular, magnets with the chiral helimagnetic order of magnetic moments. The enhanced interest in this class of substances is due to their unusual fundamental properties, as well as due to the prospects of application of these properties in spintronics, magnetic memory, and sensorics. The structure and the stability of the ground state of such a magnet can be studied by analyzing the spectrum of spin excitations against its background, which can in turn be studied through the interaction of these excitations with the system of nuclear spins. The system of nuclear spins under the conditions of nuclear magnetic resonance (NMR) is a unique source of information on the local spatial distribution of electron and spin density in a magnet. The spectrum of elementary spin excitations of the system under study has two distinctly pronounced branches: the usual spin-wave excitations (call them *d* magnons), and excitations localized on solitons (call them *w* magnons) [1,2].



In this study specific features of NMR of such systems have been studied. Within the spin-wave approximation, the following basic local characteristics of the NMR of such structure have been calculated: the NMR frequency, the frequency shift, the tensor of enhancement coefficients and the line broadening. In addition, the field and temperature dependences of these characteristics have been investigated. The magnetic resonance susceptibility of the electron-nucleus spin system has been calculated; the integral shape of the NMR absorption line has been analyzed. The problem of the evolution of the NMR absorption line upon the change in magnitude of the external magnetic field has been solved [1].The figure shows the curves of absorption and dispersion (dashed and solid curves respectively) at various values of the external magnetic field. The obtained results can be used in the study of the ground state of the new materials with modulated magnetic structure (in the case of cubic or uniaxial anisotropy), characteristic features of rearrangement of its structure in the vicinity of phase transitions and high-frequency magnetic properties [3-5].

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P 64 High-frequency low-field EPR spectroscopy of Tm^{3+} and Tb^{3+} impurity ions in synthetic forsterite

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The system of electron levels for the Van Vleck paramagnetic centers is split up to singlet states. The value of the zero field splitting (Δ) between the ground and the first excited electron states varies widely. Magnetic dipole transitions between these levels are allowed for the parallel orientation of magnetic component of the microwave field ($B_1 \parallel z$) with the change of the magnetic quantum number $\Delta m = 0$ only at relatively low magnetic field, when the Zeeman energy does not exceed significantly the value of Δ. At $g\beta B_0 >> \Delta$ the magnetic dipole transitions are forbidden. Therefore high-frequency tunable EPR spectroscopy at low magnetic field is a unique tool for the investigation the Van Vleck paramagnetic centers in solids.

The Tm^{3+} and Tb^{3+} impurity ions in synthetic forsterite have been studied experimentally in the frequency range of 180 – 300 GHz on a frequency-tunable submillimeter EPR spectrometer [1]. This spectrometer is based on tunable backward wave oscillators as a source of the microwave radiation and a wide-band quasi-optic guide. EPR spectra of Tm^{3+} and Tb^{3+} paramagnetic centers revealed a set of narrow lines in the magnetic field close to zero. This observation was unexpected because a specific feature of the Van Vleck paramagnets is the nonlinear dependence of the electron level energy on the magnetic field. In the simplest case of two isolated singlet levels their energies are given by

$$W = \pm\sqrt{\left(\frac{\Delta}{2}\right)^2 + (g\beta B)^2 |M_{12}|^2} \cdot$$

Here $M_{12} = \langle\Psi_1|J|\Psi_2\rangle$ is the matrix element of the operator of the magnetic dipole moment J mixing the ground and excited levels $|\Psi_1\rangle$ and $|\Psi_2\rangle$ in the external magnetic field. In the magnetic field close to zero the value of derivative of the dependence of the resonant frequency on the magnetic field is very small. Therefore the magnetic field modulation does not change the electron level energy and does not modulate the resonant conditions. The origin of the narrow lines in the low-field EPR spectra is discussed.

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P 65 Reducing the charging effect during construction of nanopillars with e-beam writing and imaging on highly insulating substrates

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Electron beam (e-beam) writing of highly insulating samples has charge accumulation which reveals reduction pattern resolution, positioning and imaging during writing process. In this work, we fabricated $Co_2MnSi/Ag/Co_2MnSi$ nano pillars that are grown on highly insulating MgO substrates to investigate spin transfer torque switching and spin transfer torque oscillation properties. High charging problem that pose an obstacle during the e-beam writing process and scanning electron microscope (SEM) imaging, was solved without using conducting polymers that may destroy physical and chemical properties of Co_2MnSi Heusler Alloy.

P 66

First-principles calculations of delafossite-like systems MCrS$_2$ and CuMnO$_2$

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Physical properties of strongly frustrated systems are of great interest for last few decades. The delafossite-like structures are one of classes of such materials. They contain 3d magnetic ions surrounded by ligand octahedra, which form triangular layers separated by nonmagnetic ions. Due to the frustration inherent to triangular geometry the magnetic properties in these compounds are quite unusual.

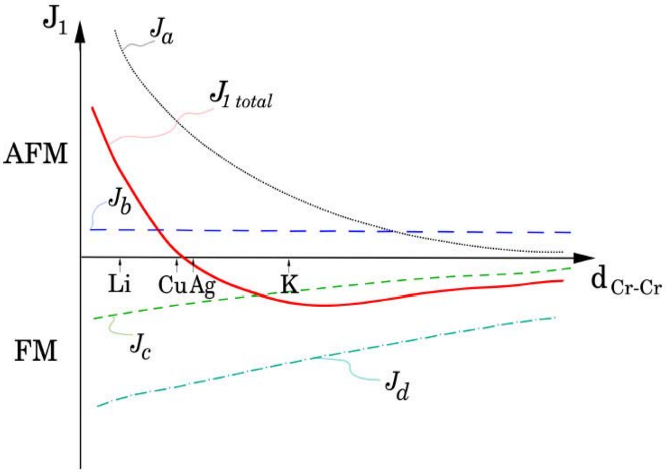

Fig.1. Schematic dependence of the contributions to the exchange between nearest-neighbor Cr ions in MCrS$_2$ on the Cr-Cr distance: J_a - the exchange part due to direct overlap of t$_{2g}$ orbitals; J_b and J_c - parts, given by exchanges between the same (J_b) and different (J_c) t$_{2g}$ orbitals through 90^o Cr-S-Cr angle; J_d - FM part to the total exchange caused by hopping from half-filed t$_{2g}$ orbital to empty e$_g$ orbital.

We perform ab-initio band structure calculations of two delafossite-like systems: MCrS$_2$ (where M=K, Na, Li, Ag, Au) [1] and CuMnO$_2$ [2] in the framework of LDA+U approximation. At low-temperature phase the magnetic moments on Cr^{3+} (d^2) in AgCrS$_2$ are organized in double chains in CrS$_2$ plane, it is a very rare configuration. The main feature in CuMnO$_2$ is behavior of the exchange interaction between neighboring triangular MnO$_2$ layers. With the small substitution of Mn^{3+} (d^4) by Cu^{2+} (d^9) the antiferromagnetic exchange between neighboring Mn planes becomes ferromagnetic. The magnetic properties of these systems have being explained by analysis of the exchange interaction constants for the Heisenberg model using the Liechtenstein approach (LEIP) [3] in MCrS$_2$ and the total energy differences for different magnetic structures in CuMnO$_2$. The dependence of different contributions to the Cr-Cr nearest-neighbors exchange interaction from the Cr-Cr bond length, which plays a crucial role in the formation of magnetic structure in MCrS$_2$, is shown in Fig.1. The results of this work will be useful for further experimental and theoretical investigations of systems with similar structure.

This work was supported by the projects RFFI 13-02-00374 and MK-3443.2013.2.

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P 67 Evolution of magnetic copper complexes in $Pb_5Ge_3O_{11}$ with anionic defects

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Authors of [1-3] investigated the a- and b-centres of doubly-charged copper in lead germanate by EPR method. It was demonstrated that a-centres are Cu^{2+} ions substituting Pb^{2+} ions which are located in positions with C_3 symmetry (at room temperature), and are displaced in the plane perpendicular to the C_3 axis and form three triclinic centers. As a result of rising of jumps frequency between three non-central configurations at temperature above 350K, a-centers form single axial spectrum [2-3] with principal magnetic axis parallel to C_3. Triclinic b-complexes show magnetic axes orientations and spin Hamiltonian parameters close to ones for a-centers, but don't show interconversion [1].

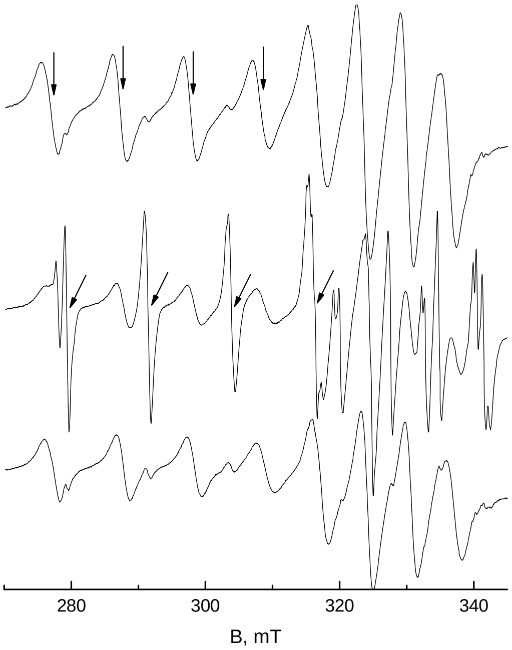

Fig.1. Part of $Pb_5Ge_3O_{11}$:0.06%Cu EPR spectrum at 300 K at $B \| Z \perp C_3$ (Z – principal axis of one of three Cu^{2+} b-centres). Inclined arrows indicate b-centre hyperfine quartet signals and vertical arrows indicate ^{63}Cu isotope a-centre. 1 – original sample, 2 – annealed in chlorine-containing atmosphere, 3 - annealed in chlorine-containing atmosphere, and then in air.

In this work we experimentally investigated change of a- and b-centres concentrations at annealing of the nominally pure crystals and crystals doped with Gd^{3+}, Fe^{3+} and Cu^{2+} in chlorine-, bromine- and fluorine-containing atmosphere as well as at different oxygen pressure (see Fig.1). We found the existence of several types of b-centres and determined parameters of their spin Hamiltonians.

We considered mechanisms of change of a charge state of copper ions and interconversion of a-and the b-centres. In our opinion b-centre is a noncentral Cu^{2+} ion in a trigonal Pb^{2+} position (or a-centre) which is stabilized in one of triclinic configurations by presence of anion at one of interstices of the next empty channel.

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P 68 The paramagnetic resonance of pair centres of rare-earth Gd^{3+} ions in lead germanate

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In EPR spectra of all $Pb_5Ge_3O_{11}$ crystals doped with gadolinium (0.01-0.1 mol.%), in a vicinity of 1/2↔-1/2 transition of the trigonal centre Gd^{3+} at $B||C_3$ the symmetric group of satellites is observed (see fig.). The intensity ratio of these satellites to signal of single Gd^{3+} ion are about 10^{-4} and linearly depends on gadolinium concentration in crystal. According our papers, in lead germanate Gd^{3+} ion substitutes Pb^{2+} only in one site of hexagonal cell with parameters c=10.685Å and a=10.251Å [1]. Therefore in this crystal there can not be pair centres of Gd^{3+} with distance smaller than 10Å.

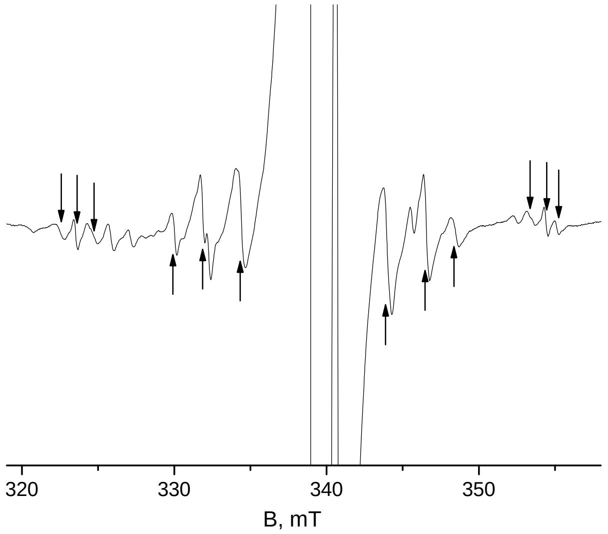

Fig.1. EPR spectrum in vicinity of 1/2↔-1/2 transition of Gd^{3+} trigonal centre at $B||C_3$ and 130 K. The top arrows mark transitions of Gd^{3+} ion pairs with axis $||C_3$, bottom arrows - with axis $\perp C_3$. In the spectrum there are also transitions of the Gd3 centers Gd^{3+}, Gd^{3+}-Cl^-, Cu^{2+}, Mn^{2+} and not identified signals.

To calculate spectrum of Gd^{3+} ion pairs we take into account a fine structure of a single ion, a full Hamiltonian of magnetic dipole-dipole and isotropic exchange interactions. For this purpose we created the computer program which builds energy matrix of 128th order and finds its eigenvalues. The program was tested by comparison of results with reported in works [2-3].

We perform calculation of spectrum and its orientation behaviour for two closest pairs. The interaction parameter is chosen according to structural data stated above. As a result, it is shown that observed satellites (marked by arrows in Fig.1) belong to transitions of pairs, and isotropic exchange interaction parameter of Gd^{3+} ions does not exceed 1MHz.

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P 69 On the use of low-field NMR full FID method for quality control in food industry

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One multi-pulse sequence like CPMG**,** but at step by step increasing intervals τ_i between 180°-pulses [1], was used to measure full FID curve (FID plus echo amplitudes):

$$90°\text{-FID}\tau_0\text{-}(180°\text{-}\tau_1\text{-echo-}\tau_1\text{-})_{\mathbf{N1}}\text{-}\Delta\tau_1\text{-}(180°\text{-}\tau_2\text{-echo-}\tau_2\text{-})_{\mathbf{N2}}\ldots\text{-}\Delta\tau_{(j)}\text{-}(\text{-}\tau_{j+1}\text{-}180°\text{-}\tau_{j+1}\text{-})_{\mathbf{Nj+1}}\,, \qquad (1)$$

where $\tau_{i+1} = \tau_i + \Delta\tau_i$. Such pulse train has a lower number of 180° pulses than regular CPMG, and avoids the "heating" of the sample and the "saturation" of the spin system by reducing the RF power absorbed by the sample during the experiment. This allows to determine the amplitudes of the mobile components having long NMR relaxation times more accurately.

Peanuts, almonds, cedar nuts, soy flour, cellulose filters and other products were investigated. NMR relaxometer "Hromatek-Proton-20M" with resonance frequency 20 MHz, duration of 90^o-pulse 2,2 μs, and "dead time" 10 μs, was used for measurements. For example, pulse sequence parameters were: $\tau_0 = 40\mu s$; $\tau_1 = 40\mu s$, $N_1 = 20$; $\tau_2 = 250\mu s$, $N_2 = 20$; $\tau_3 = 1ms$, $N_3 = 20$; $\tau_4 = 4ms$, $N_4 = 150$. Fast part of FID has been digitized in a range from 10μs to 40μs every 0.5 microseconds. All amplitudes of the echo signals were measured at the maxima on width 10μs. Small number of data points significantly accelerates mathematical processing of the experimental results, that is very important for the continuous monitoring in industry. Equation (2) has been used as the fitting function:

$$\frac{A(t)}{A_0} = P_1 \frac{\sin bt}{bt} \exp\left(-\frac{t^2}{2T_{21}^2}\right) + P_2 \exp\left(-\frac{t^2}{2T_{22}^2}\right) + \sum_{k=3}^{n} P_k \exp\left(-\frac{t}{T_{2k}}\right). \qquad (2)$$

For dry products P_n are generally characterized by the content of protein (P_1), residual moisture (P_2), saturated and unsaturated fatty acids ($P_3 - P_5$), etc.

The method improves the accuracy of determining the relative amplitudes of the relaxation components, because the effects of the instability of resonance conditions, of the gain of the receiver and the baseline drift is lower than at the separate measurement. Processing of the FID and CPMG echo signals was used.

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P 70 Anisotropy of Mn-Mn exchange interaction in paramagnetic phase of $LaMnO_3$: ^{17}O NMR

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The oxide $LaMnO_3$ is a key system for experimental and theoretical studies that aim to resolve the relative importance of the electron-electron and electron-lattice interactions for the orbital physics of manganites [1].

According to [2,3] the cooperative Jahn-Teller (JT) distortions in $LaMnO_3$ disappear at $T > T_{JT} = 750$ K and the long-range orbital order (OO) removes. The crystal structure at $T > T_{JT}$ appears almost cubic on average [3], while dynamical JT distortions of the MnO_6 octahedra remain up to about 1150 K [4]. The OO provides an anisotropy of the effective exchange interaction [5], which explains the A-type antiferromagnetic spin order below $T_N \sim 140$ K [6]. In the paramagnetic phase, this static spin order transforms into a time-fluctuating short-range spin order of Mn neighbors so that no valuable information on the anisotropy of the effective exchange interactions can be obtained above T_{JT} from bulk magnetic and transport measurements of intrinsically twinned $LaMnO_3$ crystals. In this work, we resolve issues about the Mn-Mn spin correlation anisotropy and its variation across the orbital order - orbital disorder transition in $LaMnO_3$ by means of ^{17}O NMR.

In orthorhombic (*Pbnm* space group) $LaMnO_3$ there are two structural oxygen sites: O1 along the *c* axis and O2 in the *ab* plane. The pathway of the superexchange (SE) interaction between two Mn neighbors involves O1 and O2 sites. The nuclear spin, ^{17}I, probes the unpaired electronic spins of Mn^{3+} ions through the transferred hyperfine interactions, which traces properties of the SE interaction at each site.

The ferromagnetic nature of the SE coupling between Mn spins in the *ab* plane is confirmed up to T_{JT}, whereas along the *c* axis, SE is antiferromagnetic up to ~550 K and alters gradually toward FM-type with further heating, resulting in an anisotropic-to-isotropic change of the exchange coupling with reinforced ferromagnetic correlations above T_{JT}. Furthermore, the ^{17}O spin-spin relaxation time, $^{17}T_2$, shows also the differences of low-frequency dynamics of the Mn spins at the O2 and O1 sites. At the O2 site, $^{17}T_{2,O2}$ is almost constant up to T_{JT}, while at the O1 site, $^{17}T_{2,O1}$ data indicate the thermally activated slow fluctuations of Mn spins along *c* axis above ~550 K. Such behavior of Mn spin fluctuations means that collective modes of adjacent MnO_6 octahedra should be considered for this slow mechanism which yields changes of spin correlations between Mn neighbors along *c* axis.

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P 71 Magnetic properties of organic metal κ-$(BETS)_2Mn[N(CN)_2]_3$ studied by dc magnetization, magnetic torque and NMR.

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A comprehensive study of magnetic properties including dc magnetization, magnetic torque, and ^1H and ^{13}C NMR measurements has been performed for organic conductor κ-$(BETS)_2Mn[N(CN)_2]_3$. At ambient pressure this material undergoes a metal-insulator transition at $T_{MI} \approx 25$ K, while the external pressure of ~0.5 kbar recovers the normal state down to $T_c \approx 5$ K where the system becomes a superconductor. According to ^{13}C NMR and the magnetic torque data, the transition of the system into the insulating state is followed by localization of the conduction π-electron spins into an antiferromagnetic (AF) long-range ordered state characterized by a canted structure due to Dzyaloshinskii- Moriya interaction and having an unusually high spin-flop field ~7 T. By contrast, the state of 3*d* Mn^{2+} electron spin moments below T_{MI} is neither a long-range AF nor purely paramagnetic. It is likely that the manganese subsystem forms a kind of a frozen tilted structure that may signify its trend to an AF order which is frustrated geometrically by the triangular arrangement of Mn in the anion layer. This result suggests that the MI transition in κ-$(BETS)_2Mn[N(CN)_2]_3$ is not the consequence of the interactions within the Mn^{2+} spins but due to the interactions within the π-electron system itself.

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Electrochemical properties and activation of organonickel sigma-bonded complexes of type [NiBr(aryl)(N-N)]

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The organonickel complexes of type [NiBr(aryl)(N-N)], where aryl – 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp), N-N – 2,2’-bipyridine, 1,10-phenanthroline are important key intermediates of various homo- and cross coupling process catalyzed by nickel complexes [1]. However, in some cases additional activation of these species is required in order to increase an efficiency of the catalytic process. In this respect a search for new methods of its activation is one of the priority goals of modern chemistry and catalysis.

It this work we report the investigation of electrochemical properties of organonickel complexes using methods of cyclic voltammetry and *in situ* EPR-spectroelectrochemistry.
It was experimentally found that these species can be easily activated electrochemically. According to *in situ* EPR-spectroelectrochemical study an electron transfer to the molecule of organonickel complex leads to formation of coordinatively unsaturated [Ni(aryl)(N-N)] radical specie with unpaired electron localised predominantly on the diimine ligand (Fig.1) [2].

$$[\text{NiBr(aryl)(N-N)}] + \text{e} \longrightarrow [\text{NiBr(aryl)(N-N)}]^{\bullet -} \longrightarrow [\text{Ni(aryl)(N-N}^{\bullet})] + \text{Br}^{-}$$

aryl = Mes, Tipp; N-N = bpy, phen

Fig.1. The mechanism of electrochemical activation of organonickel complexes [NiBr(aryl)(N-N)].

This electrochemical technique allows elaborating new methods for activation of organonickel sigma-bonded complexes strongly increasing their reactivity in electrocatalytic reactions of C-C and P-C bonds formation [3].

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^{1}H NMR of water colloidal solutions of nanosized crystalline particles $LaF_3:Gd^{3+}$

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The magnetic resonance imaging (MRI) has a wide range of applications in medical diagnostic. To increase the quality and quantity of obtained information the contrast agents are used. It helps to determine the location of the affected area and its characteristics. The most commonly used intravenous contrast agents are based on chelates of gadolinium. We synthesized the series of nanosized LaF_3 and $LaF_3:Gd^{3+}$ samples and investigated them by nuclear magnetic resonance.

Colloidal water solutions of nanosized crystalline particles of LaF_3; LaF_3 with 20 minutes hydrothermal treatment; LaF_3 doped with Gd^{3+}; LaF_3 doped with Gd^{3+} with 20 minutes hydrothermal treatment were prepared. Concentration of Gd^{3+} in respective solutions was 15.9 mM/L. NMR signals of protons were registered by Chromatech 20M NMR spectrometer. Water solutions at different concentrations were prepared and ^{1}H relaxation rates were measured. For comparison, characteristics of the commercial preparations Magnevist®, Gadovist® were used. As a result relaxation rates of LaF_3 doped with Gd^{3+} are higher than those of commercial preparations (Fig.1).

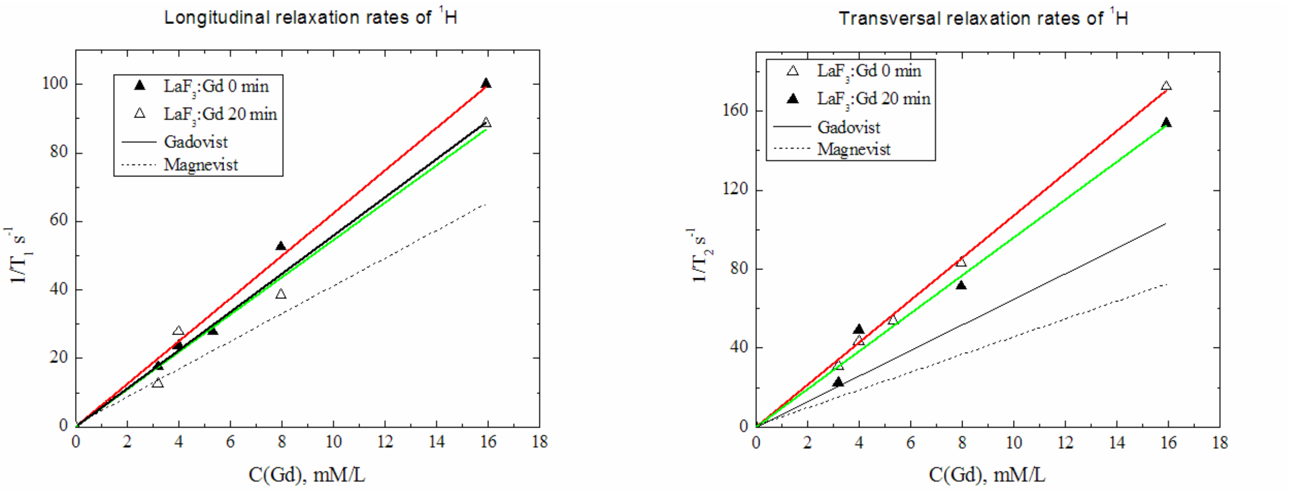

Fig.1. T_1 and T_2 relaxation rates of protons for $LaF_3:Gd^{3+}$ solutions with different concentrations of Gd^{3+} and commercial preparations Magnevist®, Gadovist®. The experiment was carried out at temperature of 37^0C.

P 74 EPR of octahedrally coordinated Mn^{2+} ions in semiconducting PbTe: Manifestation of pseudo-Jahn-Teller effect

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Lead chalcogenides PbS, PbSe and PbTe ($A^{IV}B^{VI}$) are narrow gap semiconductors with a strong ionic character of the bonds and have the rocksalt structure. They have a small band gaps, a high static dielectric constant, large carrier mobility and a positive temperature coefficient of the gap ($dE/dT > 0$). Their direct band gap occurs at the L point in the Brillouin zone. These characteristics make them unique among polar compounds and have important applications in infrared devices and thermoelectric materials.

Today studies about heterostructures, films, quantum wires and quantum dots or wells of lead chalcogenides cause much attention to the physical properties of the lead chalcogenides, especially, to magnetic properties of the materials doped by paramagnetic impurities such as manganese, chromium, iron, and so on.

A very interesting results on investigations of undoped PbTe crystals were reported in [1]. The highly unusual ferroelectric fluctuations in PbTe revealed in the work [1] were interpreted in [2] as abnormally large-amplitude thermal vibrations which could arise due to a delicate competition of dual ionicity and covalency. Such fluctuations put PbTe near ferroelectric instability and produce anomalous properties such as partially localized low-frequency phonon modes, a soft transverse optical phonon mode, and a positive temperature coefficient for the band gap.

The purpose of the present work was a study of the ferroelectric instabilities in the PbTe semiconducting crystal by EPR method. Impurity Mn^{2+} ions embedded into lattice of crystalline PbTe were used as paramagnetic probes. $Pb_{1-x}Mn_xTe$ samples were grown by Bridgman method in quartz crucibles. Concentration of the manganese impurity was varied in the interval $0{,}001 < x < 0{,}02$. The samples were mounted in a two-circle goniometer and rotated in the (110) and (001) crystallographic planes. The measurements were carried out at X-band region at liquid helium temperature (4.2 K). Six principal Mn^{2+} hyperfine lines were observed in the EPR spectra. The field intervals between the lines were found to be isotropic under rotation in the (110) plane within the experimental error of about 0.1 G. Each of these hyperfine lines was found to be surrounded by satellite lines attributed to fine structure of EPR spectra of the centers under investigation. Observed EPR lines had a Dysonian shape.

In some details our results are like those got in [3]. But the observed angular dependences in the fine structure of EPR spectra cannot be accounted for neither by static model of cubic Mn^{2+} center nor by static trigonal Mn^{2+} center. To describe experimental results of the present investigation the dynamic pseudo-Jahn-Teller model with the coupling $(A_{1g}+T_{1u})\times(a_{1g}+e_g+t_{1u}+t_{2g})$ scheme is considered [4] where A_{1g} corresponds to the ground ^6S term of Mn^{2+} and T_{1u} accounts for a vibronic mixing of exited states.

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P 75 NMR evidence for zinc-induced dimerization of beta-amyloid peptide metal binding domain with English mutation.

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Alzheimer's disease (AD) is caused by abnormal aggregation of β-amyloid peptide (Aβ), an endogenous product of the proteolytic cleavage of the amyloid precursor protein (APP). Full length Aβ contains 40 to 42 amino acid residues, including the metal-binding domain (1-16) and the hydrophobic tail (17-42). A key pathogenic process in the AD onset is transition of water-soluble Aβ monomeric molecules into neurotoxic oligomers, followed by formation of insoluble fibrillar aggregates. Zinc and copper ions play a critical role in this pathological transition, since Aβ oligomerization is started by metal ion interaction with the Aβ metal binding domain. The APP gene mutations leading to amino acid substitutions in the Aβ molecule may increase its ability to aggregation. English familial mutation (H6R) which is located within the metal-binding domain of Aβ was recently shown to accelerate amyloid fibril formation, causing early AD development.

In order to reveal the molecular mechanism of the accelerated aggregation of Aβ-H6R, we studied zinc interaction with the metal binding domain Aβ(1-16)-H6R using the methods of NMR spectroscopy, molecular dynamics, and quantum mechanics. It was found that Aβ(1-16)-H6R forms a stable dimeric complex in the presence of zinc ions. The zinc binding stoichiometry, a set of amino acid residues involved into the zinc binding, and the parameters describing exchange between monomeric and dimeric forms of the zinc-peptide complex were determined using various NMR techniques. High resolution spatial structure of the dimeric form of Aβ-(1-16)-H6R complex with zinc ion in water solution was determined from the NMR data and subsequently refined using the QM/MM calculations (Fig. 1). A family of the final 20 NMR conformers has been deposited to the Protein Data Bank (PDB id 2MGT).

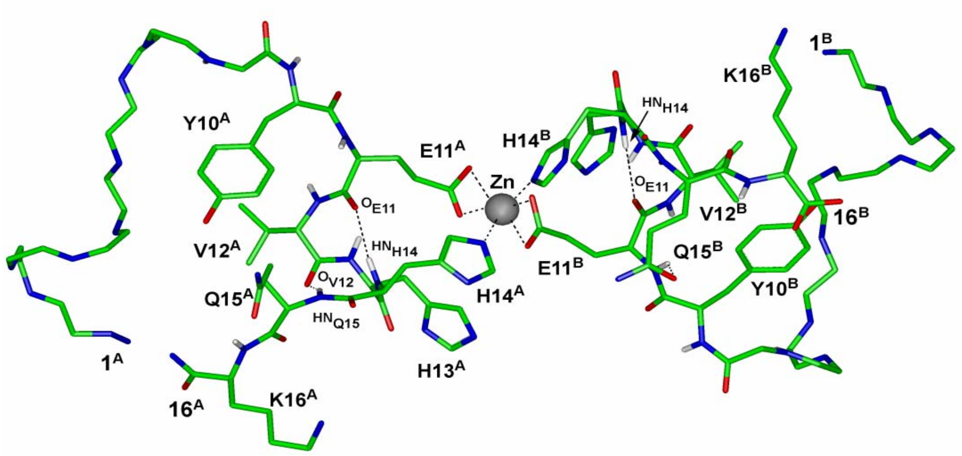

Fig. 1. Representative conformer of the complex of Aβ(1-16)-H6R dimer with a zinc ion.

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P 76 EPR and NMR study of ion-exchanged mordenites

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Zeolites have a number of interesting, even unique properties, which may be utilized in various areas, especially in heterogeneous catalysis [1]. In the past few years it has been shown that the introduction of copper in the zeolite structure significantly improves the catalytic performance of the system [2]. Despite a considerable amount of both experimental and theoretical works, a fundamental and comprehensive understanding of intrinsic mechanisms that govern the catalytic processes in these materials still merits complementary investigations. Electronic paramagnetic resonance (EPR) is a powerful tool to study the copper ion state in zeolites [3,4]. Magic angle spinning nuclear magnetic resonance (MAS NMR) helps to test the Al/Si framework imperfection caused by ion-exchange processes [5,6]. Here we report on the results of our complementary study of protonated and copper-exchanged zeolites with mordenite structure and with the molar SiO_2/Al_2O_3 ratio equal to 10 (samples HMor10 and CuMor10, respectively).

EPR studies of the hydrated CuMor10 sample showed that copper ions are in the Cu^{2+} state ($g_{xx}(g_{\perp}) = 2.115 \pm 0.001$, $g_{yy} = 2.120 \pm 0.001$, $g_{zz}(g_{||}) = 2.370 \pm 0.001$; $A_{xx} = 48 \pm 1$ MHz, $A_{yy} = 3 \pm 1$ MHz, $A_{zz} = 410 \pm 1$ MHz**)**.

^{27}Al MAS NMR studies showed that in HMor10 about 15% of Al atoms are six-coordinated that means the aluminum-silicon framework is rather imperfect. Substitution Cu^{2+} for H^+ leads to the framework recovery. Thermogravimetric analysis showed that such a substitution changes both the character and the temperature of the adsorbed molecules release.

To treat experimental data we have calculated the geometry and electronic structure of $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_4]^{2+}$ clusters (both free and incorporated into the zeolite matrix). Comparison of calculated and measured parameters of the hyperfine interaction tensor allowed us to make a conclusion about the coordination of Cu^{2+} ions in the mordenite lattice.

The studies were performed at the resource centers of Saint-Petersburg State University: Centre for Magnetic Resonance, Center of X-ray diffraction studies, Centre of Thermal Analysis and Calorimetry, Computer Center.

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Quantum and classical correlations in the solid-state NMR free induction decay.

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Quite recently applications of the NMR spin dynamics to investigate quantum information processing were initiated [1]. It is usually assumed that the quantum correlation existing both at low and high temperatures influence the performance speed of quantum computer [2]. On the other hand different time correlation functions (TCF) define observed NMR signals in conventional NMR. However their decomposition in quantum and classical components has not been done yet. In the present note it will be done for one of the most significant NMR TCF, namely, for the free induction decay (FID) function. As it was shown earlier [3] the FID shapes for the systems of classical magnetic moments and for quantum spins ones coincide if there are many quite equivalent nearest neighbors *V* in a solid lattice.

Let's turn the equilibrium nuclear magnetization to a plane perpendicular to external magnetic field by the radio frequency pulse and then expand the density matrix $\rho(t)$ with respect to the complete system of orthogonal operators $[k)$ [4, 5]. By this way we get TCF $A_k(t)$ as amplitudes describing the evolution of system. If to follow a standard procedure [2, 6] we have to reduce $\rho(t)$. It means that fixing two spins *i* and *j* we have to calculate the trace over all other spins. So for the large number of neighbors and at high temperatures we get

$$\rho_{ij}(t) \approx (2S+1)^{-2}[1+\beta A_0(t)(S_{xi}+S_{xj}) - \beta A_1(t)3b_{ij}(S_{yi}S_{zj}+S_{yj}S_{zi})].$$

Here b_{ij} is the dipole-dipole constant, S is nuclear spin number. $A_0(t)$ is a FID and $A_1(t) = \dot{A}_0(t)/M_2$, $M_2 = 3S(S+1)\sum_j b_{ij}^2$. Hence for the mutual information which represents the measure of correlation [2] we gain

$$I(\rho_{ij}) \approx \beta^2 b_{ij}^2 [S(S+1)\dot{A}_0(t)]^2 /(M_2^2 \ln 2).$$

According to a general theory [2] one has to process a measurement at $\rho_{ij}(t)$ to extract classical correlations. To do it we can exploit the method developed in [7]: we need to use the orthogonal measurement of von Neiman if S=1/2 and the generalized POVM measurement using the set of spin coherent states for S>1/2. As a result we calculated a portion of quantum correlations:

$$D_{ij} = I(\rho_{ij})/2 \text{ if } S = 1/2 \text{ and } Q_{ij} \approx I(\rho_{ij})/(S+1) \text{ if } S > 1/2.$$

Our results mean that in spite of coincidence of the FID shapes both of classical and quantum spin systems for a large number of nearest neighbors [3], the quantum properties of the system are not lost. For every pair of spins the portion of quantum correlations changes from 1/2 to 1/(S+1) with S growing up. So quantum properties disappear completely only if $S \rightarrow \infty$ and not in the case when $V \rightarrow \infty$.

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P 78 EPR study of the photodynamic processes in fluoride crystals activated by rare earth ions

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Generation of laser radiation in ultraviolet spectral range in RE-activated dielectric crystals is strongly limited by photodynamic processes such as excited-state absorption, colour centres formation and destruction, recombination and charge transfer processes and so on [1, 2]. However, exact mechanisms and characteristics of these processes, which would allow minimizing their deteriorating influences or even using them to the benefit of the developed quantum electronic devices, such as solid-state saturable absorbers, are not yet well described. Thus, colourcentres change their characteristics under the influence of the external factors such as temperature or additional irradiation of active medium [3]. Besides, so far F^- centres in $LiY_{1-X}Lu_XF_4$ crystals were being assigned referring to the interpretation of the ESR spectra performed in [4], still there is no similar findings as to the other types of colour centres in these materials.

Monocrystals of the fluoride crystals doped with Ce^{3+} ions (0.2 - 1 at.%) were synthesized using Bridgeman-Stockbarger technique in the laboratory of crystal growth of KFU. The samples were cut for EPR measurements to approximately 3 x 3 x 3mm^3 sizes with principal axes of the samples perpendicular to the cut planes. Observation of the photodynamic processes was performed using modified X-band EPR spectrometer Bruker ESP 300. The light excitation was performed either using Perkin-Elmer xenon arc lamp or using modulated laser beam at 266, 355 and 532 nm. The influence of the laser irradiation on EPR spectra was detected using lock-in amplifier Ametek 7270 SR.

Whereas at T=300K the EPR transitions of Gd^{3+} were observed, at T=10 K additional signals of Er^{3+}, Yb^{3+}, Ce^{3+} were found. Applying the optical radiation leads to the variation in the EPR lines intensity of these ions. The observable processes had quite slow dynamics compared to the relaxation time of the Ce^{3+} ions (~30 ns). The first reason might be related to the ionization with following reduction of Ce^{3+} ions due to excited state absorption processes during irradiation. The other possibility is formation and bleaching processes of colour centres of various natures, resulting in the charge transfer to Ce^{3+} ion.

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Nuclear polarization and relaxation in Si:P at ultra-low temperatures

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Dynamic nuclear polarization (DNP) is an important tool in magnetic resonance, which provides versatile control of the nuclear polarization and substantial enhancement of the sensitivity of NMR. Very interesting systems where the effects of DNP can be studied are shallow donors (P, As, Bi) in Si. Magnetic resonance studies of these samples have a long history starting from pioneering work of Feher [1]. Recently the interest to this system has been raised by the proposal of Kane [2] to utilize these impurity atoms for quantum computing with the nuclear spin serving as a memory qubit and electron spin for readout.

In this work we report on the details of the experimental study of DNP of ^{31}P donors in silicon (Si:P) performed in strong magnetic field and temperatures below 1K. At these conditions donor electron spins are fully polarized, electron and nuclear relaxation times are extremely long. All these factors substantially change the efficiency of DNP: pumping with extremely low RF powers ($<1\ \mu$W) for reasonably short time ($\approx$1 hour) very high values of DNP ($>98\%$) of ^{31}P were reached. The DNP has been obtained via the Overhauser effect by pumping allowed ESR transitions followed by the cross relaxation via the flip-flip and flip-flop transitions. We evaluated the corresponding cross relaxation times and discuss the dependence of the DNP on the pumping time.

We performed detailed study of the nuclear relaxation of ^{31}P donors in the temperature range 0.75-2 K. The relaxation did not follow a single exponential dependence of time, but is quite well described by the bi-exponential function. Both relaxation times have exponential dependence on 1/T with the electron Zeeman energy in the exponent, which indicates on the Nuclear Orbach mechanism of relaxation.

We also realized a resolved solid effect in Si:P by pumping the ^{31}P-^{29}Si forbidden electron-nuclear transitions. As a result we observed a pattern of narrow holes and peaks in the ESR spectrum, corresponding to polarization of ^{29}Si in the specific lattice sites, resolved due to the superhyperfine interactions ^{31}P-^{29}Si. This opens a way of using large ensembles of identical ^{29}Si nuclei for quantum computing.

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